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INSTITUTE OF FUNDAMENTAL STUDIES

FINAL REPORT ON

PHOTOFIXATION OF DINITROGEN ON SEMICONDUCTOR CATALYSTS

(USAID-PSTC 936.5542, AID.SCI.8.269)

Principal Investigator-O.A.Ileperuma

Division of Physical & Chemical Sciences
Institute of Fundamental Studies
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Covering period July 26, 1988 - June 30, 1992.

Submitted to the office of the Science Advisor
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PHOTOFIXATION OF DINITROGEN ON SEMICONDUCTOR CATALYSTS

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Division of Chemical & Physical Sciences
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1. Executive Summary

This project envisages the development of semiconductor based catalysts for the conversion of gaseous nitrogen to ammonia using light as the energy source. Although several attempts have been made to employ semiconductors to carry out this process, the yields of ammonia are far too small to be of any practical significances. This project attempts to modify semiconductor catalysts to enhance the nitrogen reduction ability by varying preparation procedures, manipulating particle sizes and preventing undesirable side reactions. One particular side reaction, viz. the photooxidation of ammonia to nitrate has been exhaustively studied because of its strong effects on catalytic activity.

It was found that the catalyst preparation conditions play a crucial role in determining the activity of the catalyst. Furthermore, it is possible to enhance nitrogen reduction to ammonia by micromolecular engineering methods. Some of these include the preparation of colloidal and quantum sized particles of semiconductors such as iron and titanium oxides, rare-earth metal hydroxides and also supported catalysts on such supports as clays and Nafion films. As a result of these investigations, the yields of ammonia have been increased by nearly 50 fold when compared to the yields obtained by others. Thus concentrations of ammonia in excess of 100 μmol l^{-1} could be obtained with the best photocatalysts developed. Furthermore, with the system of Q sized hydrous ferric oxide particles embedded in a Nafion matrix, simultaneous oxidation and reduction of nitrogen photocatalytically to ammonium and nitrite ions was observed. The yields obtained in this case are typically in the 100-150 μmol l^{-1} range which merits further research in this area.

The present work contributes to the global research efforts in the chemical conversion of solar energy to a useful product. Although the development of a practical nitrogen fixing solar cell requires the concerted efforts of scientists worldwide, our results hopefully provide a fresh awareness in the area of solar energy conversion.

The training given to junior scientists and the general scientific awareness created have been advantageous from the point of view of overall development of the LDC concerned.

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2. Research Objectives

Nitrogen fixation on irradiated semiconductors is an attractive possibility of utilizing solar energy to produce an important product. However, this research which attracted scientists after the oil crisis of 1973 is currently not under active investigation. The reason for this is the realization that yields obtained were often in the μmol range (10^{-6} molar range) and hence of no practical significance. However even if the quantum yields are small, if they can be improved to at least about 100 μmol l^{-1}, a possibility exists for developing a nitrogen fixing solar cell. The difficulties in getting good yields of NH_3 arise from (a) the high activation energy of the reaction (b) poor chemiadsorption of N_2 on the surfaces (c) back reactions and photooxidation of NH_3 to NO_3^- which poisons the catalysts and (d) loss of catalytic activity with time. The present study was undertaken with a view to comprehensively study the basic physics and chemistry of this process and to improve the yields obtained in the photoreduction of N_2 to NH_3.

The objectives set in the Research proposal submitted to AID/SCI on "Photofixation of Dinitrogen on Semiconductor catalysts" can be briefly summarized as follows:

1. Identification of new semiconductor catalysts for photocatalytic N_2 fixation.

2. Improvement of the ferric oxide system as a N_2 reduction catalysts.

3. Increasing the N_2 fixing ability by optimizing the conditions in the catalyst preparation.

4. Determining the dependance of band gap on particle size.

5. Determination of the flat band positions of semiconductors depending on the method of catalyst preparation.

6. Studying the adsorption and oxidation of NH_3 on photocatalysts and how this affects catalytic activity.

7. Investigating catalyst poisoning and approaches to overcome the factors responsible for poisoning.

8. Development of a practical N_2 fixing solar cell.

This report describes the research undertaken on this project and how the above objectives were reached. Many new catalytic systems were exhaustively studied and the mechanisms understood. The results obtained were also of some significance to the knowledge in an allied field, viz. photosplitting water to hydrogen. When world wide attention has been diminishing on research involving chemical means of solar energy conversion, the information gathered during the course of this research could still lead to a practically viable system in a few decades.

3. Methods and Results

This section briefly discusses a summary of the important results obtained for the various catalysts employed. Full experimental details and a detailed discussion of the results obtained are given in the next section.

3.1 Hydrous ferric oxide based catalysts

Very early in our research on photofixation of N_2, we discovered that N_2 reduction takes place on hydrous ferric oxide (1). It was also found that dried or calcined Fe_2O_3 is inactive as a photocatalyst, contrary to the observations of others (2,3). The catalytic activity in this case is attributed to its strongly negative flat band potential position coupled with the strong chemisorption of N_2 on the catalyst surface. Here nitrate formed by the photooxidation of NH_3 as the reaction progresses has a detrimental effect on catalytic activity as seen form the loss of activity with time. Nitrate formed in turn was found to change the flat band potential values in a less negative direction and this explains the loss of catalytic activity. In order to improve on this catalyst, the composite catalyst containing Fe(III)/Ti(IV) hydrous oxides was investigated (4). Here the nitrate formation is small and the increased ammonia yields can be attributed to the separation of charge centers.

3.1.1 $V(OH)_3/Fe_2O_3.xH_2O$ System

When the analogous Fe(III)/V(III) mixed hydroxide system was investigated, it was found that the yields of ammonia can be increased nearly 10 fold compared to hydrous ferric oxide alone. Nearly 200 μmol l^{-1} of NH_3 was obtained after 24h of irradiation. Here the possible reduction of V(III) to V(II) which is known to reduce N_2 to NH_3 in a thermal reaction (5) is perhaps responsible for the above enhancement. Such high yields in photocatalytic N_2 fixation have not been reported in the literature (6) and this gives further encouragement to continue research in this area.

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3.1.2 $Fe_2O_3.xH_2O$/Bentonite precursor pillared clays

Iron oxide supported layered clays such as bentonite were investigated for two reasons; (1) increased surface area provided by the clay layers (2) possible charge separation between hydroxylated iron oxide strands and the clay layer. The precursor pillared clays with polymeric Fe(III) hydroxo species had an ammonia enhancement factor of 3-4 over hydrous ferric oxide as a photocatalyst.

3.1.3 FeOOH fine particles

Photohydrolysis of iron(II) bicarbonate produces ultra-fine particles of FeOOH and its blue shifted spectrum is a consequence of size quantization effect (7). Again we have noted that N_2 is not reduced by Fe^{2+} or $Fe(OH)_2$ in the presence or absence of light in contrast to observations of previous workers (8). Again, $Fe(OH)_2$ efficiently reduces nitrates and nitrites quite effectively in a thermal reaction. Thus traces of these ions present as impurities may very well have been the origin of NH_3 described in reference 8. Work on hydrous ferric oxides also have some relevance to prebiotic chemistry where photocatalytically active iron(III) oxide particles may have been effective in promoting N_2 fixation and other reactions.

Fine particles of FeOOH produced are active in photogenerating NH_3 from N_2. The yield of ammonia reaches an optimum value of ca. 60 μmol l^{-1} and even after 24h of irradiation, there was no decrease in the yield which is an inherent disadvantage with most of the catalysts studied. Hydrogen evolution also takes place with high efficiency here with nearly 10 ml of H_2 generated within 2 h. Thus these quantum sized particles of FeOOH presents a formidable catalyst and a promising system for future studies.

3.1.4 Q-particles of $Fe_2O_3.xH_2O$ in a Nafion matrix

Out of all catalysts studied during the course of this project Q-particles of hydrous ferric oxide on Nafion films has the best potential for a practical device. An ideal device for N_2 fixation should have the ability to use air and water to generate nitrogenous fertilizer. Hydrous iron(III) oxide loaded Nafion films in aerated water

at alkaline pH yields both NH_3 and NO_2^-/NO_3^- upon UV irradiation. Thus the potential of using such films for a practical device to produce ammonium nitrate cannot be dismissed. Q-particles of hydrous iron oxide embedded in these films have an average diameter of ~48 Å, show size quantization effects in the UV-VIS spectra and have a flat-band potential more negative than any of the iron oxide systems studied. The microenvironment of the Nafion matrix probably suppresses O_2^- formation thereby reducing photooxidation of NH_3 to NO_3^-. This prevents catalyst deactivation and hence we observe that the total N_2 fixed, both reductively and oxidatively increases with time and shows no decrease at least up to 60h of continuous irradiation.

3.1.5 Some mechanistic aspects

Some details of the mechanistic aspects of the N_2 reduction on semiconductors can be obtained by studying both N_2 fixation and water splitting reactions simultaneously. Irradiation of a semiconductor produces electron hole pairs.

$$Fe_2O_3 \longrightarrow Fe_2O_3^{\bullet}\ (h^+, e^-) \qquad (1)$$

The photoexcited electrons can reduce either N_2 or H_2O.

$$N_2 + 6H^+ + 6e \longrightarrow 2NH_3 \qquad (2)$$

$$H_2O + 2e \longrightarrow OH^- + H_2 \qquad (3)$$

Photogenerated positive centers, h^+ (holes) oxidize water to oxygen or capture adsorbed OH^-

$$6h^+ + 3H_2O \longrightarrow 3/2O_2 + 6H^+ \qquad (4)$$

$$OH^- + h^+ \longrightarrow {}^{\bullet}OH \qquad (5)$$

$$2\ {}^{\bullet}OH \longrightarrow H_2O_2 \qquad (6)$$

The OH free radicals or the peroxides have enough oxidizing powder to oxidize NH_3 to NO_2^- or NO_3^- (9) An alternate mechanism for N_2 reduction to NH_3 has been suggested by Schrauzer (reactions 7-11).

$$N_2 \xrightarrow[h^+ ,2e]{TiO_2} N_2^{2-} \quad (7)$$

$$N_2^{2-} + 2H^+ \longrightarrow N_2H_2 \quad (8)$$

$$N_2H_2 \longrightarrow N_2 + H_2 \quad (9)$$

$$2N_2H_2 \longrightarrow N_2 + N_2H_4 \quad (10)$$

$$3N_2H_4 \longrightarrow 4NH_3 + N_2 \quad (11)$$

As evidence for the above mechanism Schrauzer has forwarded the enhanced hydrogen yields with these catalysts under N_2 when compared to under argon. This has been termed "Nitrogen assisted hydrogen evolution". For hydrous ferric oxides and its derivatives studied, although hydrogen evolution has been well established, only traces or no oxygen could be found (gas chromatography using molecular sieve column, membrane polarographic detector). However we have consistently observed the formation of peroxides (acidified KI solution followed by colorimetric estimation). This is consistent with the observations of others where the photouptake of O_2 on hydrous ferric oxide has been demonstrated. with the Fe_2O_3/ bentonite catalyst, we have also observed N_2 assisted H_2 evolution where higher H_2 yields were observed under N_2 compared to Ar at higher durations of irradiation.

3.2 Metal doped Titanium dioxide catalyst systems

3.2.1 Introduction

The first experiments that titanium dioxide (rutile) converts N_2 to NH_3 were carried out by an Indian chemist, Dhar nearly four decades ago. He showed that river sands rich in rutile have the ability to convert N_2 to NH_3 when exposed to tropical sunlight (10). However this result was largely ignored by the Western scientists until 1977 when Schrauzer proposed that TiO_2 and its metal doped modifications produced traces of hydrazine and ammonia upon exposure to UV radiation under N_2(1). The photocatalytic nature of this process has been questioned (11). Furthermore we have found along with others (6) that TiO_2 by itself produced only

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negligible amounts of ammonia. It is also difficult to assess the work of most workers in this area since experimental details such as the removal of traces of NH_4^+ and NO_3^- from reagents used are not properly described. Although some isotopic work using $^{15}N_2$ confirm N_2 fixing activity, comparisons of quantum yields are also difficult due to lack of relevant data. Furthermore most of the work has been carried out on samples of TiO_2 heated at 1000°C and no optimization with respect of the conditions on the preparation of catalyst have been made. Detailed investigations were made to optimize NH_3 yield by varying factors such as dopant amount (percentage of doping), heating temperature and duration of heating. In addition, variation of NH_3 yield with pH has also been studied. The observed catalytic activities for NH_3 formation were correlated to the position of the flat band potentials. The positions of both the conduction band and the valence bands were obtained from the combination of Mott-Schottky plots and reflectance measurements (Eg).

The catalysts were characterized from X-ray powder diffraction patterns, UV-Vis reflectance spectroscopy, FT-IR spectroscopy measurements. Photosplitting of water on all catalyst systems was also studied and its relationship to N_2 fixation was investigated.

3.2.2 RuO_2/TiO_2 system

Compared to photoreduction of N_2 to NH_3, there is little work reported on oxidative nitrogen fixation reactions on semiconductor surfaces. Bickley (12) has reported the photooxidation of N_2 to NO on irradiated rutile while Schrauzer has reported the photooxidation of initially formed NH_3 to NO_2^- on Fe-doped rutile (13). Since the photooxidation of NH_3 on irradiated rutile is well known (14) it is surprising that not much attention has been paid to this process by workers in this area.

Photoreduction of N_2 to NH_3 on ruthenium doped rutile has been reported (15). However we have found that more NO_3^- is obtained with this catalyst compared to NH_3. This is not surprising since RuO_2 is widely used as a hole transfer agent in semiconductor catalysis. There was no significant difference when nitrogen is replaced by air in these experiments. This suggests that the photooxidation of NH_3

with either hydroxyl free radicals or peroxide is the preferable pathway compared to direct oxidation of NH_3 with O_2. Oxidative nitrogen fixation also takes place on irradiated ZnO where peroxide generation upon UV irradiation is well established (16).

3.2.3 Mg/TiO_2 System

With this catalyst system optimization of preparation conditions with respect of catalytic activity was achieved by varying the following; dopant concentration, dopant amount, doping temperature, doping time and pH. It was found that the optimum conditions are; dopant amount 2%, doping temperature 1000°C, doping time 2h and a pH of 10. The yields of NH_3 were smaller compared to hydrous iron oxide systems. The yields reach a maximum value of ~ 15 μmol l^{-1} after 2h and decreases thereafter.

Experiments on this catalyst system emphasizes the importance of controlling the conditions of preparing the catalyst. Heating at 500°C at best produces only surface doping which however seems to produce more active catalysts than heating at 1000°C where lattice doping takes place. Doping of Ti^{4+} in TiO_2 with a metal ion having a lower charge has been attempted as a possible way to increase catalytic activity towards water splitting (17). Apparently more surface defects are created and this could increase the adsorption capacity of substrates on the catalyst surface. Doping with Mg^{2+} creates a narrower depletion layer width which affects the rate of band bending. This would allow electron tunnelling to proceed more easily at the interphase thereby enhancing electron transfer.

3.2.4 V/TiO_2 and Ce/TiO_2 Catalyst systems

These systems clearly demonstrate the need to optimize the catalyst preparation conditions to achieve highest N_2 reduction ability. The optimum conditions in the preparation of the catalysts are summarized in the following table.

Catalyst	Dopant amount	Heating Temperature/°C	Duration of Heating/h	pH
V/TiO_2	10	750	4	3
Ce/TiO_2	10	250	2	12.5

Table. 1 Optimum catalyst preparation conditions for V/TiO_2 and Ce/TiO_2 Catalysts.

The ammonia yields from these catalysts were considerably higher when compared to similarly constituted metal doped TiO_2 systems reported by other workers. This may be due to the formation of reduced cerium and vanadium centers by the injection of photoexcited electrons of TiO_2. These reduced centers such as Ce^{3+} and V^{2+} have sufficient redox potentials to reduce N_2 via a thermal pathway. Again these catalysts are active for the photoreduction of water to H_2. Their flat-band potential positions too have been studied and these correlate well with their observed catalytic activity towards N_2 reduction and photogeneration of H_2.

3.2.5 WO_3/TiO_2 composite catalyst system

It has been shown that the reaction of moist N_2 on blue substoichiometric tungsten oxides ($WO_{2.96}$) in the solid phase gives NH_3 upon irradiation. In aqueous solution reduction of N_2 to NH_3 takes place via a thermal reaction. This reaction reported by Bard (18) can be written as,

$$WO_{2.96} + 0.04H_2O + (.04/3)\ N_2 \longrightarrow WO_3 + (0.08/3)NH_3$$

We accidently observed that hydrous tungsten oxide, $WO_3.2H_2O$ in contact with TiO_2 left in sunlight turned blue due to the reduction of WO_3 to the substoichiometric blue form, $WO_{2.96}$. Measurement of the flat band potential positions enables one to understand the above reaction. Since the conduction band of TiO_2 which is at -0.70 V (vs NHE) lies above the conduction band position of

WO_3 (-0.45 V vs NHE), photoexcited electrons in TiO_2 can be transferred to WO_3 thereby reducing it. Thus in principle a cyclic system for the photogeneration of NH_3 is possible.

3.3 Sm(III) and Eu(III) Hydrous Oxides

Prompted by the activity of the hydrous iron oxides and its derivatives, a systematic search was made to identify other hydrous oxides with similar activity. After examining a large number of such hydrous oxides we have found that those of samarium(III) and europium(III) are also active for the photoreduction of N_2 to NH_3. Here too, the ammonia concentration rapidly increases in about 4-6 h and then gradually decreases. The nitrate concentration in the solution shows an exactly opposite behaviour. Dried catalysts of Sm_2O_3 and Eu_2O_3 are completely inactive towards N_2 reduction activity. The flat-band potentials indicate a slightly more negative value for the conduction band position of both catalysts. These hydrous oxides presumably adsorb N_2 well similar to the hydrous ferric oxide systems studied.

3.4 DETAILED DESCRIPTION OF THE RESULTS

Most of the work carried out under this project have either been published or submitted for publication. The papers which follow give the full experimental details and a critical analysis of the results in relation to those in the literature and our own work. In addition to the N_2 reduction process, we have studied the parallel pathway of photocatalytic water reduction. The desirable properties of a suitable photocatalyst for a practical device are also dealt with.

Nitrogen photoreduction by V (III) substituted hydrous ferric oxide

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Abstract

Hydrous ferric oxide where Fe (III) sites are partially substituted by V(III), suspended in nitrogen purged water is found to photoreduce nitrogen to ammonia. It is suggested that this system gives significant yields of ammonia because photogenerated holes are efficiently scavanged by V^{3+}.

Introduction

Several workers have reported the detection of nitrogen reduction to ammonia in irradiated aqueous dispersions of TiO_2 purged with nitrogen [1-6]. Nitrogen chemisorption on the surface of the catalyst in an essential requirement for the reaction. The author and his collaborates have found that hydrous ferric oxide which chemisorbs nitrogen better than TiO_2 is more effective photocatalyst for nitrogen reduction [7]. In photogeneration of hydrogen from water, using semiconductor catalysts, it is well known that dissolved electron donor sacrificial agents [8] give much higher yields of hydrogen. Here the efficient consumption of holes by the sacrificial agent, greatly enhances electron transfer to water. One could expect that the same strategy is applicable in improving the ammonia photogeneration rates in nitrogen purged aqueous semiconductor suspensions. Contrary to the above expectation, we have noted that the addition of water soluble electron donors (e.g. organic compounds/reducing ions etc.) completely suppresses the ammonia production. The obvious explanation is that, the sacrificial agent in solution interferes with chemisorption of nitrogen on the surface of the catalyst (Generally N_2 is poorly chemisorbed and readily replaced by other species in the solution). One way to overcome this problem; would be to have a solid sacrificial agent in contact with the active catalyst. If holes are transferred to this solid sacrificial agent, nitrogen reduction will be enhanced. We have found that N_2 photoreduction with hydrous Fe_2O_3 can be enhanced by incorporating vanadium (III) hydroxide which act as hole scavenger.

Experimental

The composite system containing $Fe_2O_3.nH_2O$ and $V(OH)_3$ was prepared as follows. Solutions of Fe^{3+} and V^{3+} (0.1M $FeCl_3$ and VCl_3) were mixed in different proportions and made alkaline to pH of 8; when a greenish brown precipitate is formed. Precipitate is washed avoiding air contamination and stored in deareated water. Photolysis experiments were carried out in an water cooled (26°C) immersion well type photochemical reactor (Applied Photophysics) of volume 400ml. 400W medium pressure mecurry lamp is housed inside the inner double walled quartz cylinder. The

precipitate containing 3.6 moles of (V+Fe) suspended in 350ml of water (pH adjusted 8 with NaOH) placed inside the reactor is kept purged with 99.99% nitrogen (bubbling rate $10 ml^{-1}$). Aliquots of solution drawn from the reactor at different irradiation intervals were tested for ammonia (indophenol blue method). Outgoing gas was estimated for hydrogen by gas chromatography (Shimadzu GC-9AM, Molecular sieves 5A column). Blank experiments were also conducted by keeping the lamp switched off with N_2 purging and with the lamp switched on under Ar purging. Ammonia concentration in the solutions obtained from the blank experiments was negligible (ie $< 1\ \mu mol l^{-1}$). Extreme precautions were taken to avoid ammonia contamination. All chemicals used were tested for ammonia and nitrate.

Results and Discussion

Fig. 1 illustrates the time development of the ammonia concentration during irradiation. Compared to pure $Fe_2O_3.nH_2O$ the yield is much higher. An optimum is reached in about 8h and thereafter the ammonia concentration decreases. The decrease in the ammonia concentration possibly results from inactivation of the N_2 reducing capacity followed by photodecomposition of ammonia. Fig. 2 shows the variation of the optimum yield with V/Fe ratio in the precipitate. The maximum yield is obtained when Fe/V ~ 1. Fig. 3 shows hydrogen evolution from the system during photolysis. Initially Ar purged solution give slightly more hydrogen than N_2 purged solution. Later stages, more hydrogen is obtained from N_2 purged solution. It is likely that ammonia photodecomposition is releasing hydrogen after deactivation of the ammonia synthesis. Mixing of Fe^{3+} and V^{3+} solutions generate an equilibrium mixture containing Fe^{3+}, Fe^{2+}, V^{3+} and V^{4+} (and perhaps VO^{2+}) ions. Addition of NaOH to the mixture produces a composite precipitate containing $Fe_2O_3.nH_2O$, V_2O_3,nH_2O, $Fe(OH)_2$ and $VO(OH)_2$ [$V(OH)_4$ is unstable]. We believe that the active component in the precipitate $Fe_2O_3.nH_2O$, where Fe^{3+} substituted by V^{3+} to some extent. Isomorphous substitution is possible, because Fe^{3+} and V^{3+} have nearly identical ionic radii. Of the

photogenerated carriers in the mixed hydroxide holes could be captured by V^{3+} sites on surface via the reaction

$$V^{3+} + h^{+}(VB) \longrightarrow V^{4+}$$

$$V^{4+} + 4H_2O \longrightarrow V(OH)_4 + 4H^{+} \qquad (1)$$

$$V(OH)_4 \longrightarrow VO(OH)_4$$

The reaction product disproportionate into $VO(OH)_2$ and water. Electrons accumulating will reduce chemisorbed nitrogen to ammonia, ie

$$N_2 + 6H^{+} + 6e^{-}(CB) \longrightarrow NH_3 \qquad (2)$$

A schematic diagram illustrating the reaction mechanism is shown in Fig. 4. When the precipitate is prepared using Fe^{2+} and V^{3+} solutions, the nitrogen reduction activity is drastically reduced showing that a ferric component is necessary for the high activity. Again pure $V(OH)_3$, $Fe(OH)_2$ or a mixture of $Fe(OH)_2$ and $Fe_2O_3.nH_2O$ are completely inactive towards N_2 photoreduction. Furthermore if Fe^{3+} and V^{3+} hydrous oxides are separately prepared and then mixed activity is again lowered. Above facts suggest that the hydrous ferric oxide where Fe^{3+} sites are substituted to some extant by V^{3+} is responsible for the reaction. The pH of the solution is found decrease during photolysis as expected from the reaction (1).

Figure captions

Fig. 1 Time development of the ammonia yield during photolysis. (a) Composite precipitate (b) Pure hydrous ferric oxide.

Fig. 2 The variation of the optimum yield of ammonia with the V/Fe ratio in the precipitate.

Fig. 3 Hydrogen evolution during photolysis under (a) N_2 purging and (b) Ar purging.

Fig. 4 Schematic diagram illustrating the reaction mechanism.

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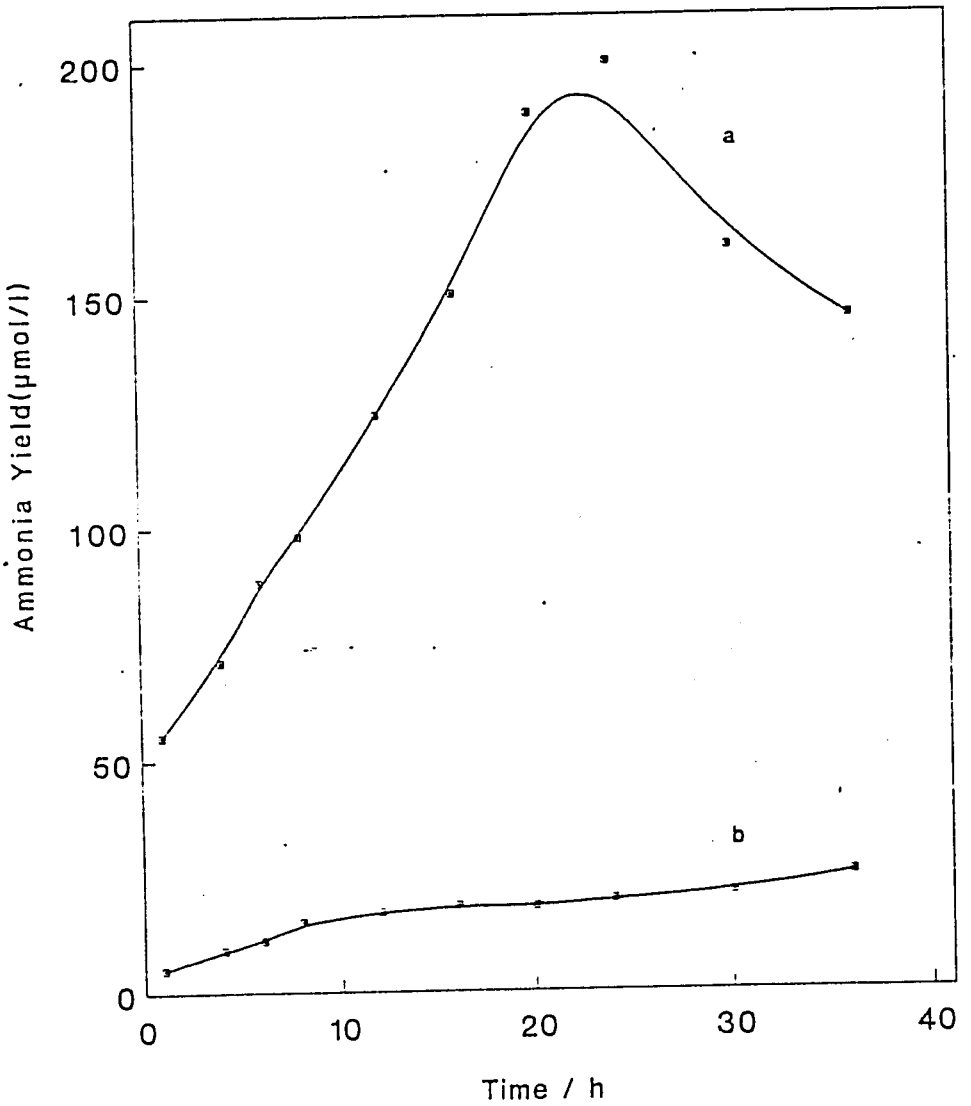

Fig.1

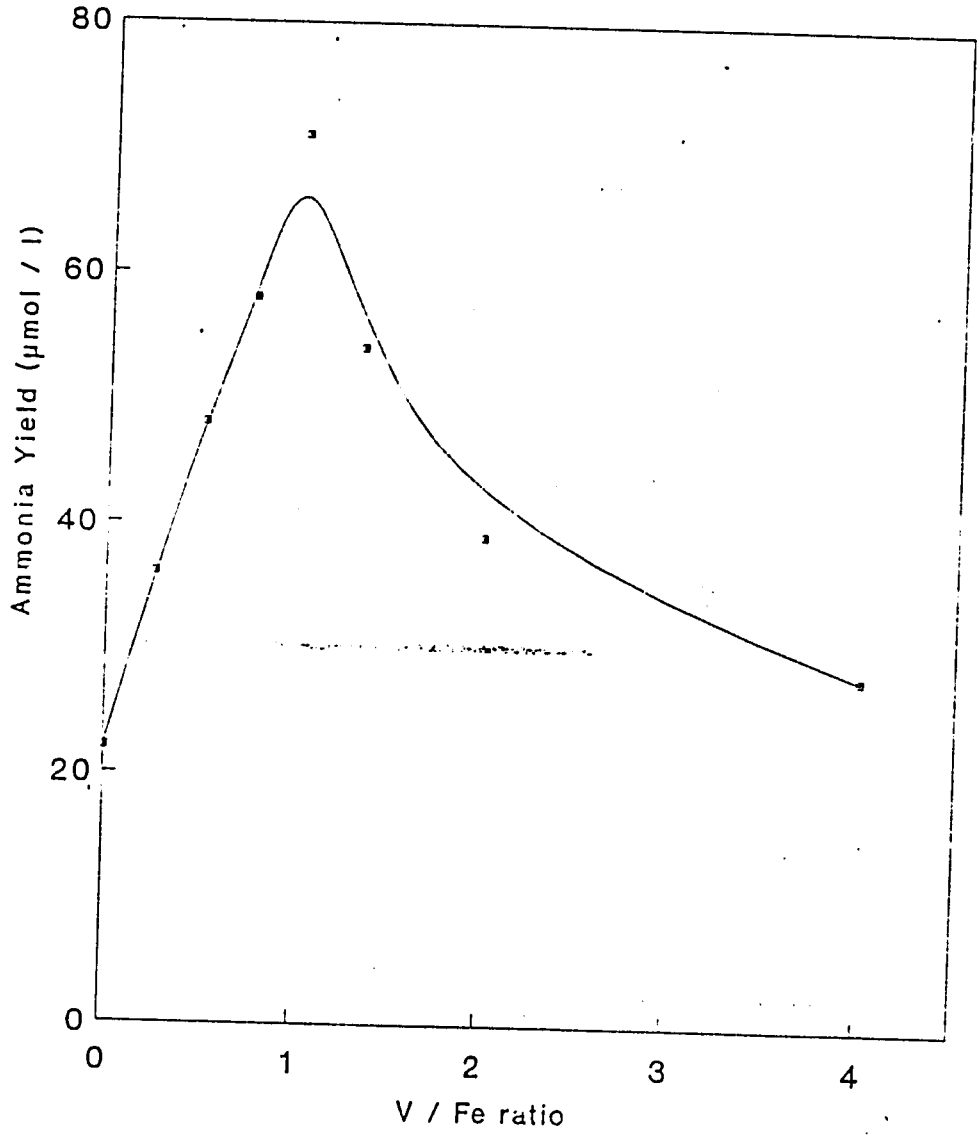

Fig. 2

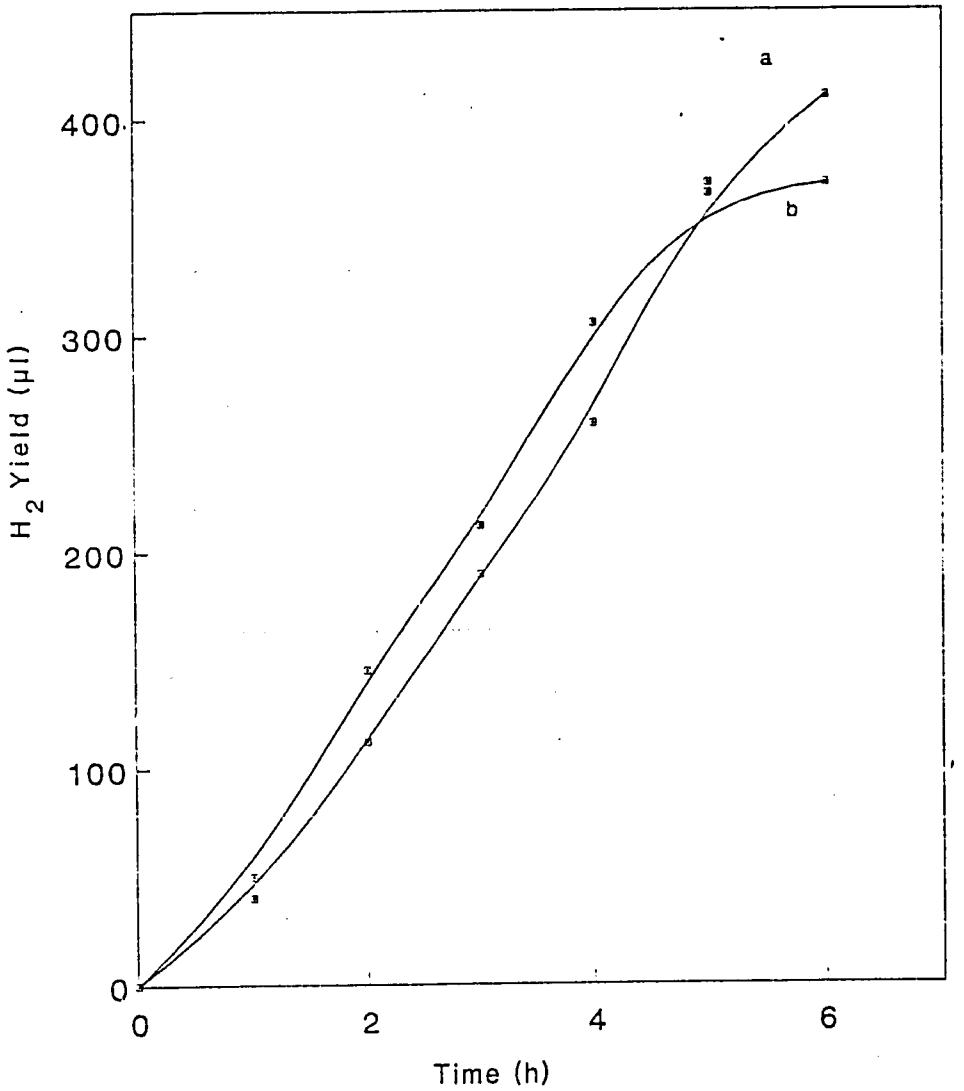

Fig. 3

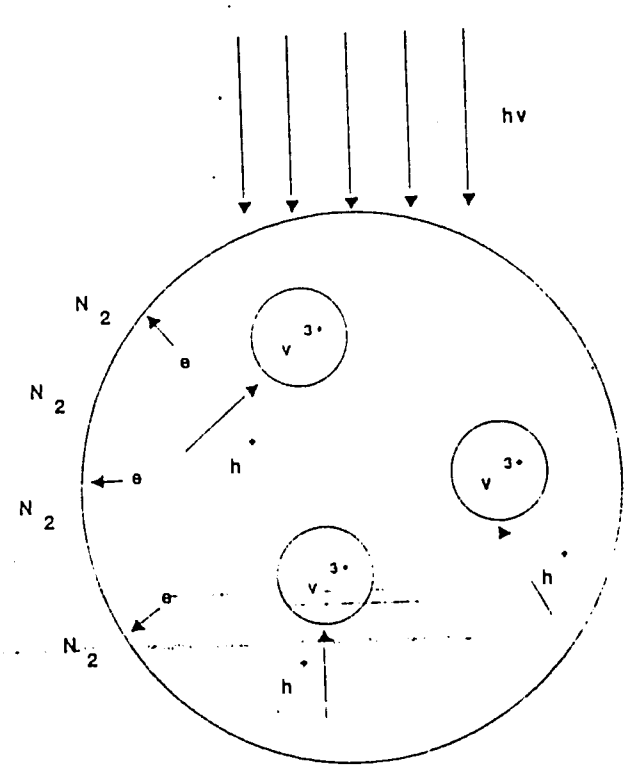

Fig. 4

J. Photochem. Photobiol. A: Chem.,

Photoreduction of nitrogen and water on montmorillonite clays loaded with hydrous ferric oxide

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Abstract

Montmorillonite clays with interlamellar cations replaced by oligomeric hydrous ferric oxides convert nitrogen to NH_3 and H_2O to hydrogen with higher efficiencies than hydrous ferric oxide alone. The enhanced activity is attributed to the larger surface area presented by the clay and to the retardation of NH_3 photo-oxidation.

1. Introduction

Clays are a class of stable aluminosilicate materials which readily disperse in water, possess large surface areas and catalytic activity [1, 2]. The montmorrillonite clays, in particular, exhibit the ability to form pillared compounds when the interlamellar cations in the clay are replaced with bulky polymeric inorganic cations followed by calcination. Such pillared clays have applications as industrial catalysts [1] in the petroleum industry. Semiconductors such as ZnS and CdS when loaded onto montmorillonite suspensions photogenerate hydrogen [3] in the presence of a sacrificial donor.

The photoreductions of nitrogen to NH_3 and H_2O to hydrogen on semiconductor-based catalysts have been studied [4] as possible means of solar energy conversion to give useful products. However, the quantum efficiencies reported for such processes are too low to be of any practical value. Furthermore, in the photoreduction of nitrogen, the yields of NH_3 reach a maximum at about 1–2 h followed by a decrease in catalytic activity. This arises due to competing reactions, such as the photo-oxidation of the NH_3 formed, and catalyst poisoning. We have previously reported [5] the photoreduction of nitrogen to NH_3 on hydrous ferric oxide using visible light. Here, the catalytic activity is due to the strongly negative flat band potential and the strong chemisorption of nitrogen on the small hydrous oxide particles. However, even with this catalyst, the NH_3 yields decrease during long-term irradiation. It has also been observed [6] that partial loading of the ferric oxide with Ti^{IV} results in enhanced yields of NH_3 with no nitrate observed up to 12 h of irradiation. Here, the possible separation of active sites for hydrogen and oxygen evolution has been suggested as the reason for the enhanced NH_3 yields obtained. A similar effect is observed when montmorillonite clays such as bentonite are loaded with hydrous forms of ferric oxides to form precursor pillared clays. Furthermore, such catalysts are also active for photogenerating hydrogen from H_2O under non-sacrificial conditions.

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2.6

2. Experimental details

2.1. Preparation of catalysts

Bentonite (BDH grade) was suspended in water and the supernatant suspension was separated from the heavier fraction. This suspension was centrifuged for 1 h at 2000 rev min^{-1} and warmed with Al–NaOH to remove all traces of NH_4^+, NO_2^- and NO_3^-. The resulting solid was then thoroughly washed with dilute acid and deionized water. The analytical grade reagents employed were also purified in a similar manner. Iron-loaded bentonite clays were prepared by two different methods. In method (a), a sol form of colloidal Fe^{III} hydroxo complexes was prepared and loaded onto bentonite; in method (b), ferric ions adsorbed onto bentonite were converted to hydrous ferric oxide.

(a) A portion of 10 ml of 0.2 M $FeCl_3$ solution was stirred at 80 °C, followed by the slow addition of a solution of 0.2 M NaOH until the molar ratio of $FeCl_3$ to NaOH reached a value of 1:2.5. This resulted in the formation of a wine red solution which is presumed to be polymeric Fe^{III} hydroxo species. This solution was added to 100 mg of the purified clay and stirred overnight. At this stage all the iron in the solution was adsorbed onto the clay. The precipitate obtained was separated by centrifuging and washed several times with deionized water until there was no trace of NH_4^+, NO_3^- or Cl^- in the washings.

(b) Clay-supported hydrous ferric oxide catalysts were prepared in a slightly different manner. A suspension containing 5 g of the purified bentonite clay in 200 ml of 0.1 M $FeCl_3$ was stirred for 24 h. The resultant Fe^{3+}-exchanged clay was then treated with an excess of 0.1 M NaOH. The solid obtained was separated by centrifugation and washed thoroughly lose their activity on drying, they were stored under water.

2.2. Irradiation procedure

Iron-loaded bentonite clay catalysts (200 mg) were suspended in 100 ml of double-distilled water in an Applied Photophysics immersion well photochemical reactor of 125 ml capacity. The lamp used was a 125 W medium pressure mercury arc lamp housed inside a water-cooled quartz jacket. The lamp emits more than 7×10^{18} photons s^{-1} cm^{-2} inside the reaction flask. Irradiation was carried out under a stream of purified nitrogen (not copper pellet column, chromic acid solution, potassium hydroxide and water). After irradiation, the mixture was distilled with 20 ml of 0.2 M NaOH and the ammonia in the distillate was determined by the indophenol blue method [7]. A portion of the catalyst suspension after irradiation was centrifuged and the nitrate content in the clear supernatant liquid was determined calorimetrically by the coupling reaction of sulphanilic acid and *N*-(1-naphthyl)ethylenediamine after cadmium reduction. Control experiments were carried out in the dark with nitrogen purging and the level of ammonia obtained here was taken as the zero standard. Control experiments carried out under argon with irradiation showed no detectable traces of NH_3 and NO_3^- under identical experimental conditions.

2.3. Hydrogen evolution experiments

Hydrogen evolution during photolysis under both nitrogen and argon was determined by gas chromatography (Shimadzu GC-9AM gas chromatograph, molecular sieve column and argon carrier gas). These experiments were independently checked by carrying out photolysis in a reaction vessel equipped with a polarographic detector (Applied Photophysics). Oxygen evolution was also tested using the same procedure.

2.4. Characterization of the catalysts

Electrochemical measurements were carried out using a Hokuto–Denko potentiostat model HA 301. This instrument was connected to a three electrode assembly consisting of a working electrode (photoanode), a saturated calomel electrode (SCE) as the reference electrode and a platinum counterelectrode. The photoanode was prepared by pressing the catalyst into a fibre glass disc. A quartz cell was used to perform the photoelectrochemical experiments and a tungsten bulb (100 W) was used as the illumination source. The cell was protected from stray light and the dark current was adjusted to zero. The photocurrent generated under continuous light chopping was biased by an externally applied potential until there was no change in the photocurrent during light chopping. The value of the externally applied voltage was then taken as the flat band potential under the particular conditions of the electrolyte employed.

X-ray powder diffraction patterns of the clay catalysts were obtained on a Shimadzu model XD-7A diffractometer using Cu Kα radiation. The particle size distributions of the catalysts were obtained with a Horiba model CAPA-700 particle size analyser using the sedimentation technique.

3. Results and discussion

3.1. Characterization of the catalysts

The wine red solution obtained by the hydrolysis of $FeCl_3$ is presumed to contain polymeric Fe^{III} hydroxo complexes with the predominant form being a dimer. When these solutions are treated with clays such as bentonite, precursors to their pillared forms are obtained. The average particle size for the bentonite precursor pillared clay with iron hydroxo species is about 0.66 μm in diameter. The X-ray diffraction patterns recorded for a clay film at 303 K exhibit a prominent peak in the region $2\theta < 10$. For bentonite this reflection (001) corresponds to a basal spacing of $d_{001} = 12.44$ Å allowing only one water monolayer intercalated between clay sheets. For the clay containing intercalated polymeric iron hydroxo species, the d_{001} spacing is 15.49 Å corresponding to two water monolayers.

The absorption spectrum of the hydrated ferric oxide was measured by reflection and exhibits an absorption threshold at approximately 595 nm corresponding to an energy gap of approximately 2.1 eV. The bentonite containing intercalated polymeric iron hydroxo species has an absorption threshold at 520 nm, which corresponds to an energy gap of 2.38 eV (Fig. 1). A similar observation has been reported by Bard [8] where the absorption edge of CdS is shifted towards the UV region on intercalation to montmorillonite clays.

Anodic photocurrents produced by the illumination of the catalyst electrode were collected by a platinum flag as described in Section 2.4. In all these experiments, potential shifts occur in the negative direction with reference to SCE. The flat band potential values become more negative with increasing pH (Fig. 2). This is similar to the shifts observed for hydrous ferric oxide which has a flat band potential of -0.34 V (*vs.* a normal hydrogen electrode at pH 11 [9]. Under these conditions, the position of the conduction band of α-Fe_2O_3, which is normally thermodynamically unsuited for hydrogen generation, becomes sufficiently negative for the photogeneration of hydrogen from H_2O [5, 9].

3.2. Photoreduction of nitrogen

The montmorillonite clays, such as bentonite, can be readily dispersed in water, possess large surface areas (approximately 750 $m^2\ g^{-1}$) with a very high cation exchange

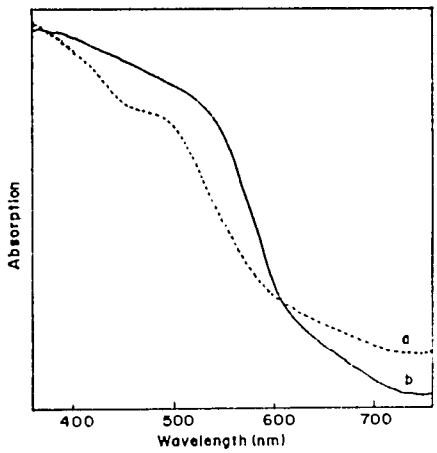

Fig. 1. Reflectance spectra of (a) polymeric iron hydroxo species adsorbed onto bentonite and (b) after heating at 250 °C for 4 h to give the pillared form.

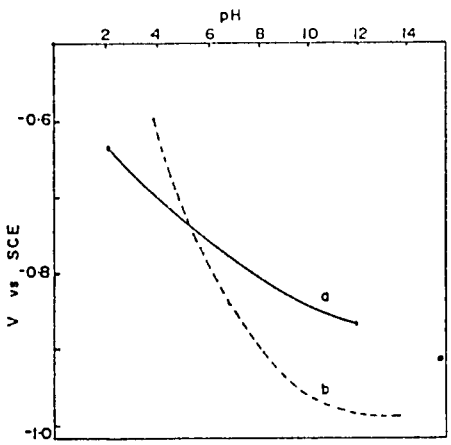

Fig. 2. Variation in the flat band potential values (*vs.* SCE) with pH of the catalysts: (a) polymeric iron hydroxo species adsorbed onto bentonite; (b) hydrous ferric oxide.

capacity (approximately 100 mequiv. per 100 g) and exhibit unusual intercalation and swelling properties [10]. These properties seem to be particularly advantageous for the preparation of efficient semiconductor-based catalyst systems. Furthermore, since bentonite is a phyllosilicate having a sheet-like structure with a negatively charged surface [11], the separation of charge carriers photogenerated on the hydrous ferric oxide may be possible. This could generate separate sites for photoreduction of nitrogen and for photo-oxidation, thereby preventing oxidation of NH_3 to NO_3^- which is

detrimental to the catalytic activity of this system [5].

Figure 3 shows the yield of ammonia and nitrate from the catalysts hydrous ferric oxide, bentonite loaded with hydrous ferric oxide and precursor pillared bentonite loaded with polymeric iron hydroxo complex at pH 10. The optimum NH_3 yields are obtained at this pH value. A feature common to all catalysts is that the NH_3 concentration in the solution rapidly increases, reaches a maximum value after 4–6 h and then gradually decreases. This decrease is followed by a concomitant slow increase in NO_3^- concentration. It is clearly seen that the NH_3 concentration for the iron-loaded bentonite systems shows an enhancement by a factor of about three. In addition, the maximum yield of NH_3 is reached after 1 h for hydrous ferric oxide, whereas for bentonite–Fe_2O_3 this period is 1 h. In the latter case NO_3^- formation appears only after 6 h. This observation supports the hypothesis that NO_3^- formation inhibits the photosynthesis of NH_3. The formation of NH_3 can be expressed by reactions (1)–(4). The quantum yields observed for NH_3 formation are in the range 0.01%–0.02%.

$$Fe_2O_3 \xrightarrow{h\nu} Fe_2O_3^*(h^+, e^-) \quad (1)$$

$$N_2 + 6H^+ + 6e \longrightarrow 2NH_3 \quad (2)$$

$$2H_2O + 2e \longrightarrow 2OH^- + H_2 \quad (3)$$

$$2H_2O + 4h^+ \longrightarrow O_2 + 4H^+ \quad (4)$$

In the case of water decomposition, multielectron transfer can be enhanced by loading the catalyst with noble metals such as platinum. However, platinization of the catalysts employed in this study resulted in a loss of catalytic activity.

The formation of NO_3^- on irradiation can be attributed to the oxidation of NH_3. This process most probably occurs via the participation of hydroxyl free radicals formed by the capture of photogenerated holes by adsorbed OH^- ions (reaction (5))

$$OH^- + h^+ \longrightarrow OH \quad (5)$$

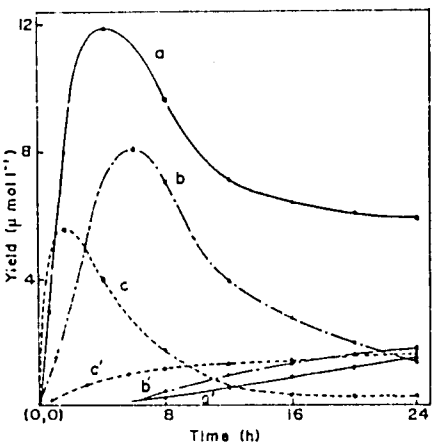

Fig. 3. Variation in ammonia (a–c) and nitrate (a'–c') yields with time for (a) polymeric iron hydroxo species adsorbed onto bentonite, (b) hydrous ferric oxide adsorbed onto bentonite and (c) hydrous ferric oxide.

The mechanism of NH_3 oxidation by OH has been deduced by flash photolysis experiments [12] and the end product has been identified as HNO. This may further react with oxygen to yield HNO_2. The oxidation of NH_3 in solution to NO_2^- during UV irradiation in the presence of semiconductors is well established [13, 14]. In our experiments, the initial formation of both NO_2^- and O_2^{2-} was detected. However, irradiation over a longer period of time caused a gradual decrease in concentration of these species, resulting in NO_3^- as the final oxidation product. Oxidation of NO_2^- to NO_3^- could take place via the involvement of photogenerated peroxide ions. Nevertheless, the extent of NO_3^- formation is less for the Fe_2O_3-loaded bentonite systems than for hydrous ferric oxide alone.

Heating the precursor pillared clays for 2 h at 250 °C results in the formation of a pillared structure of the iron oxide in the layered silicate. However, these catalysts exhibit little activity towards nitrogen reduction showing that a degree of hydration is crucial for catalytic activity.

3.3. Photogeneration of hydrogen

Figure 4 shows the yields of hydrogen obtained on irradiation (400 W mercury arc lamp) of a catalyst suspension of the bentonite precursor pillared clay containing polymeric iron hydroxo species. After 8 h, hydrogen formation is higher under nitrogen and, after 24 h, 920 μl of hydrogen are produced under nitrogen. A similar observation has been made by Schrauzer *et al.* [16] for Fe–TiO_2 catalyst and attributed to "nitrogen-stimulated hydrogen production" (reactions (6)–(8))

$$N_2 + 2e^- + 2H^+ \longrightarrow N_2H_2 \quad (6)$$

$$N_2H_2 \longrightarrow \tfrac{1}{2}N_2H_4 \quad (7)$$

$$N_2H_4 \longrightarrow N_2 + 2H_2 \quad (8)$$

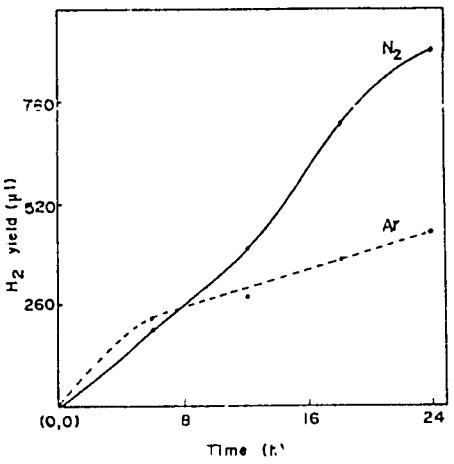

Fig. 4. Variation in hydrogen yields with time under argon and nitrogen for the bentonite catalyst containing polymeric iron hydroxo species.

Hydrogen and oxygen evolution rates were independently measured using hydrogen and oxygen electrodes and a calibrated membrane polarographic detector. Argon bubbling was carried out after each irradiation to eliminate dissolved hydrogen in the reaction medium and repeated irradiations were performed. The results show similar variations for each cycle. With the ferric oxide catalyst systems investigated, oxygen evolution is observed only after long-term irradiation. It is suggested that hydrogen peroxide is formed from OH radicals (reaction (5)) and that oxygen is formed from H_2O_2. Our results show that 3.5 μmol l^{-1} of peroxide is formed after 12 h of irradiation (colorimetric determination using I_3^- formed when these solutions are treated with acidified KI solution).

Acknowledgments

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Photoreduction of Dinitrogen to Ammonia by Ultrafine Particles of Fe(O)OH Formed by Photohydrolysis of Iron(II) Bicarbonate

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The ultrafine particles of Fe(O)OH formed during photolysis of iron(II) bicarbonate solution are found to be photocatalytically active in reduction of dinitrogen to ammonia. The method of preparation of the catalyst, ammonia yields obtained, and the reaction mechanisms are discussed.

Introduction

It is well-known that semiconductor particles have the ability to photocatalyze up-hill chemical reactions that necessitate multielectron transfer.[1,2] Although the conversion efficiencies are below the level of practical utility, photogeneration of hydrogen and/or oxygen can be accomplished with semiconductor catalysts.[1,2] There is also evidence that semiconductor particles catalyze reduction of dinitrogen to ammonia.[3-13] Several workers have reported that nitrogen purged aqueous suspensions of TiO_2 yield detectable quantities of ammonia.[3-9] The efficiency of a semiconductor catalyst depends on several factors, e.g. (1) band gap and band positions, (2) degree to which the reactants are chemisorbed on the surface of the catalyst, and (3) carrier mobility. In the case of N_2 fixation, the most severe limitation is chemisorption of N_2.[10] In an earlier work,[10] we have noted that the hydrous oxide of iron(III) is superior to TiO_2, because of its ability to chemisorb nitrogen. The activity of iron(III) hydrous oxide ($Fe_2O_3(H_2O)_n$) depends on the method of preparation which affects the particle size, the degree of hydration, and the presence of contaminants.[10,11] In this work, we describe our results on nitrogen photoreduction with a more effective iron(III) oxide catalyst prepared by photohydrolysis of iron(II) bicarbonate solution.

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Experimental Section

The difficulty of obtaining reproducible results in photoreduction of nitrogen results from contamination of the chemicals, water, and the environment with ammonia, nitrates, and nitrites (N_2 reducing catalysts will also reduce nitrates and nitrites to ammonia). Consequently, the following extreme precautions were taken. Highest quality chemicals were used and ammonia, nitrate, and nitrite contents assessed (ammonia by the indophenol blue method,[14] nitrates by cadmium reduction, and azo dye test for nitrites[15]). Iron(III) bicarbonate was prepared by the following method in a glovebox. Excess NaOH was added to a 0.5 M solution of $FeSO_4$ (AnalaR) and the mixture was boiled with pure aluminum granules. This process converts nitrate and nitrite contaminants into ammonia, which is expelled. When all aluminum is consumed, the precipitate of $Fe(OH)_2$ was washed with previously boiled 0.1 M NaOH followed by deionized distilled water and filtered. The precipitate of $Fe(OH)_2$ was transferred to another vessel containing oxygen-free water and purged with prue CO_2. When it partly dissolved to form a solution of iron(II) bicarbonate, the insoluble fraction was removed by filtration. The iron(II) bicarbonate solution prepared by this method was found to be free of ammonia and nitrates to the limit of their detectability (2 and 1 mol L^{-1} respectively for NH_3 and NO_3^-). The Fe^{2+} concentration in the iron(II) bicarbonate solution was estimated by atomic absorption spectroscopy (Shimadzu AA-670). The photon flux passing through the reactor was estimated by ferrioxalate actinometry.

Photolysis experiments were carried out in a 500-mL photochemical reactor (Applied Photophysics) with a 400-W medium-pressure Hg lamp housed in a double-walled water-cooled (26 °C) quartz cylinder. Iron(II) bicarbonate solution was contained in the annular region (~0.75 cm thickness) between the quartz cylinder and the borosilicate outer jacket. Three hundred milliliters of iron(II) bicarbonate solution ($[Fe^{2+}] \sim 1.7 \times 10^{-4}$ M) in the reactor was kept continously purged with N_2 (99.99%) and out going N_2 was passed through dilute HCl to trap any escaping ammonia. After the experiment was run for a given interval of time, photolyzed solution was made alkaline with NaOH (previously boiled to remove any NH_3) and distilled. Ammonia in the distillate was estimated by the indophenol blue method. The same procedure was adopted to estimate ammonia in the HCl trap. To estimate the error originating from ammonia contamination, blank experiments were conducted with the lamp switched off with N_2 purging and lamp switched on with Ar purging. The levels of ammonia in the distillate obtained from these experiments were comparable (~5 mol L^{-1}) and taken as

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the zero in colorimetric estimation. In a separate experiment, an iron(II) bicarbonate solution, initially purged with Ar, was also irradiated and the H_2 liberated was monitored volumetrically at atmospheric pressure by gas chromatography (Shimadzu GC-9AM gas chromatograph, carrier gas Ar, molecular sieve 5A column, thermal conductivity detector). The absorption spectra of irradiated solutions were obtained with a Shimadzu UV 3000 spectrophotometer.

Results and Discussion

It is well-known that photolysis of Fe^{2+} ion in aqueous medium yields hydrogen via the reaction[16,17]

$$2Fe^{2+} + 2H_2O \xrightarrow{h\nu} 2Fe^{3+} + 2OH^- + H_2 \qquad (1)$$

The primary reaction leading to (1) is formation of a solvated electron or a hydrogen free radical, i.e.

$$Fe^{2+} \xrightarrow{h\nu} Fe^{3+} + e^- \qquad (2)$$

$$Fe^{2+}(aq) \xrightarrow{h\nu} Fe^{3+} + H + OH^- \qquad (3)$$

Generally high pH values favor (2) and low pH values favor (3).[18] One of the factors that limit the quantum yield of hydrogen from (1) is the reverse of the reactions 2 and 3. At higher pH values (>6), Fe^{3+} formed by photooxidation undergoes hydrolysis[13,20]

$$2Fe^{3+} + 3H_2O \rightarrow Fe_2O_3 + 6H^+ \qquad (4)$$

and the net reaction becomes

$$2Fe^{2+} + 3H_2O \xrightarrow{h\nu} Fe_2O_3 + H_2 + 4H^+ \qquad (5)$$

As the back reactions of (2) and (3) are suppressed by hydrolysis of Fe^{3+}, the quantum yield of H_2 from (5) is much higher than that from (1). The spectral responses of reactions 1 and 5 are also different.[19-21] Reaction 1 is sensitive only to short wavelength UV (~240 nm), whereas reaction 3 can be carried out with long wavelength UV and near-visible (i.e. up to ~420 nm).[19,20] The difference in spectral response is attributed to presence of $[Fe(OH)(aq)]^+$ ions in higher concentrations at near neutral pH.[19] Iron(III) oxide formed via (5) is one of the hydrated forms, generally Fe(O)OH.[19] The pH of the iron(II) bicarbonate solution is in the range 5.5–6.0 and photolysis proceeeds via (5). However, there is an important difference when compared to photolysis of an iron(II) sulfate solution of equivalent $[Fe^{2+}]$ and pH (pH adjusted with NaOH). In the latter case, Fe(O)OH, which is photogenerated, rapidly coagulates and settles down. This difference could originate from the following: (1) in the $FeSO_4$ solution, the pH adjustment with NaOH always yields some iron(II) hydroxide which acts as the nuclei for coagulation; (2) the ionic concentration is higher in the $FeSO_4$ solution. Figure 1 shows the absorption spectra of a iron(II) bicarbonate solution (initially 1.7×10^{-4} M) after irradiation for different intervals of time. The position of the absorption edge is at ~390 nm and a gradual red-shift is noted with the progress of irradiation. It is important to note that the above value is much smaller than the absorption edge position of different forms of Fe_2O_3 and Fe(O)OH (hydrated and anhydrous). On prolonged standing (over 24 h) of the irradiated solution, the absorption spectrum resembles that of Fe(O)OH. The above observations suggest that during irradiation of iron(II) bicarbonate, a colloidal solution of ultrafine particles of Fe(O)OH is formed and the blue-shifted spectrum is a consequence of size quantization effect.[22,23] Figure 2 illustrates the development of the ammonia concentration during irradiation of the iron(II) bicarbonate solution kept purging with N_2. Figure 3 shows the hydrogen generation from a solution of iron(II) bicarbonate purged with Ar prior to irradiation. Initially N_2-purged solutions generate hy-

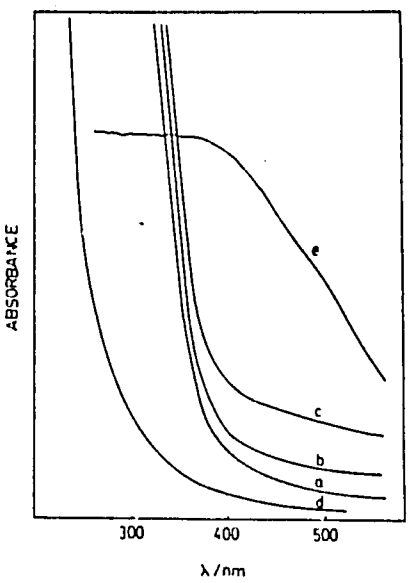

Figure 1. Absorption spectrum of a iron(II) bicarbonate solution (~10^{-4} M) photolyzed for (a) 0.5 h, (b) 1 h, and (c) 2 h, (d) absorption spectrum before photolysis, and (e) absorption spectrum of Fe(O)OH aqueous solution.

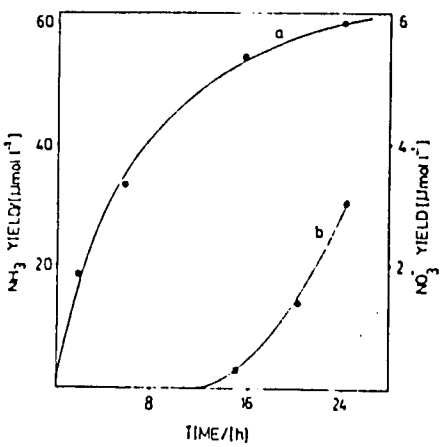

Figure 2. Time development of (a) $[NH_3]$ and (b) $[NO_3^-]$ during photolysis of the N_2 purged iron(II) bicarbonate solution (~10^{-4} M).

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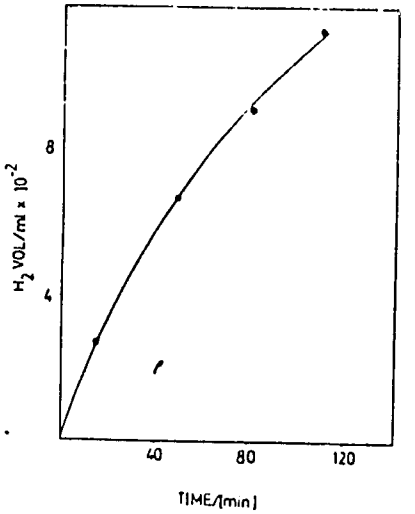

Figure 3. Photogeneration of hydrogen from a $\sim 10^{-4}$ M solution of iron(II) bicarbonate.

drogen at a rate comparable to Ar-purged solutions. However, in the latter stages of photolysis lesser amounts of H_2 were liberated from N_2 purged solutions. The yield of ammonia from the present system is higher than that from other catalysts under similar conditions.[3-13] The initial quantum yield of NH_3 in the present system is $\sim 10^{-2}$. The hydrous ferric oxide system reported earlier[10] gives quantum yields of the order 10^{-3} or smaller. Other systems reported in literature give still smaller quantum yields.[3,4,6] In a separate experiment, we found that N_2 is not reduced by Fe^{2+} ion or $Fe(OH)_2$ to any detectable extent in the presence or absence of light. (However, we found that $Fe(OH)_2$ very effectively reduces nitrates and nitrites to ammonia in a thermal reaction.) The above observations clearly prove that the ingrediant which catalyses N_2 reduction is colloidal Fe(O)OH formed by photohydrolysis of iron(II) bicarbonate. Electron and hole transfer reactions occurring at the surface of the particle would be

$$N_2 + 6H^+ + 6e^- \longrightarrow 2NH_3 \quad (6)$$

conduction band

$$3H_2O + 6H^+ \longrightarrow {}^3/_2O_2 + 6H^+ \quad (7)$$

valence band

In the initial stages of the reaction, oxygen generated via (7) could be consumed by iron(II) bicarbonate to yield Fe(O)OH. The removal of O_2 will enhance the production of ammonia due to suppression of oxidation. In fact, the nitrate level in the photolyzed solution is quite low to begin with (Figure 2) and increases on prolonged irradiation when all Fe^{2+} is consumed by photohydrolysis. The catalytic nature of the reaction is suggested by the following observation. When $[Fe^{2+}]$ is kept very low, $\sim 10^{-6}$ M, and the irradiation is continued ~ 48 h, the yield of NH_3 is found to be higher than the initial Fe^{2+} content. When a filter that cuts off light of wavelengths below ~ 300 nm is used, the NH_3 yield is drastically reduced. This observation shows that finer particles have higher catalytic activity. There has been a suggestion that precambrian banded iron oxide formations have resulted from photohydrolysis of Fe^{2+} ions in the oceans.[19-21] It is conceivable that photocatalytically active iron(III) oxide particles formed during photolysis of Fe^{2+} ions were effective in promoting other chemical reactions of prebiotic importance.

Simultaneous Reductive and Oxidative Photocatalytic Nitrogen Fixation in Hydrous Iron(III) Oxide Loaded Nafion Films in Aerated Water

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It is found that Nafion films loaded with quantum sized particles of hydrous iron(III) oxide, immersed in aerated water at alkaline pH fix nitrogen, reductively and oxidatively at the same time, in a novel photocatalytic reaction which is facilitated by the Nafion polymer matrix.

A method for photocatalytic fixation of N_2 is a demanding invention. An ideal device for this purpose should have the ability to use air and water to generate nitrogeneous fertilizer. In this communication we report our findings on a simple system which gives encouragement for practical photofixation of N_2. We have found that hydrous iron(III) oxide loaded Nafion films in aerated water at alkaline pH yields both NH_3 and NO_2^-/NO_3^- upon UV irradiation.

In all experiments, extreme precautions were taken to avoid NH_3 and NO_2^-/NO_3^- contamination. Nafion film[1,2] (Nafion 117, DuPont) cleaned by refluxing in conc. HCl and repeated washing, and boiling in distilled water was loaded with hydrous iron(III) oxide as follows: The film was immersed in 0.1 mol dm^{-3} aqueous $FeCl_3$ (pH *ca.* 1.5) for 30 min, rinsed in water and again immersed in 0.8 mol dm^{-3} NaOH for 45 min, during which quantum particles[3] of hydrous iron(III) oxide become embedded in the polymer matrix. The size of the crystallites determined from X-ray diffraction (XRD) using Sherrer's equation was *ca.* 48 Å. Extraction of Fe from a sample of the film gave the density distribution as *ca.* 2×10^{-6} Fe^{3+} mol cm^{-2}. The absorption spectrum of the film compared with that of an aqueous suspension of hydrous iron(III) oxide shows clear evidence for the size quantization blue shift[3,4] (Fig. 1).

Irradiations were carried out in a 500 ml photochemical reactor with a water cooled (26 °C) cylindrical quartz inner jacket where a 400 W medium pressure Hg lamp was housed. The Nafion film (10×20 cm^2, thickness = 0.0175 cm) was wrapped around the cylinder and tied by a thin Teflon tape. Water (350 ml; pH adjusted with NaOH) was continuously purged with purified air at a rate 10 ml min^{-1}. After running the experiment for a given time, the solution was tested for NH_3 by the Indophenol Blue method and NO_2^-/NO_3^- by azo-dye Cd reduction test. As a check on contamination, two blank experiments were conducted: (1) lamp switched-off with a coated film and (2) lamp-on with an uncoated film. NH_3, NO_2^-/NO_3^- levels in these were negligible. In another experiment the solution was purged with N_2 and Ar (99.99%) and the out-going gas examined (Shimadzu GC-9 AM). H_2 and small quantities of O_2 were detected and the yield of the latter in the Ar purged solutions was slightly higher.

Fig. 2 shows the development of the reduced ($N_R = [NH_3]$), oxidised ($N_O = [NO_2^-] + [NO_3^-]$) and total fixed ($N_T = N_R + N_O$) nitrogen concentrations in the air-purged (AP) and N_2 purged (NP) solutions. In both cases N_R increases at a decreasing rate, but quite unexpectedly AP solutions give higher yields in the initial stages of photolysis. Again NP solutions show detectable N_O only at later stages whereas the AP system gives much larger amounts of N_O from the beginning. Clearly N_R is always higher in the AP solution. Under similar conditions N_T from an equivalent quantity of bare hydrous iron(III) oxide reaches a saturation value of *ca.* 0.1 μmol l^{-1} in about 3 h.

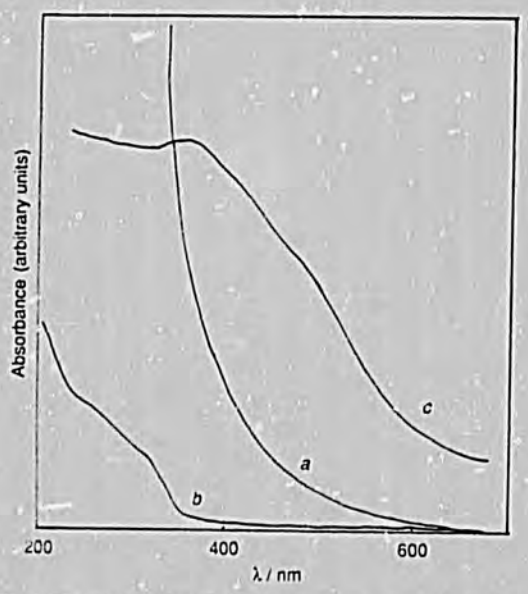

Fig. 1 Absorption spectrum of (*a*) hydrous iron(III) oxide loaded Nafion, (*b*) Nafion and (*c*) aqueous dispersion of hydrous iron(III) oxide

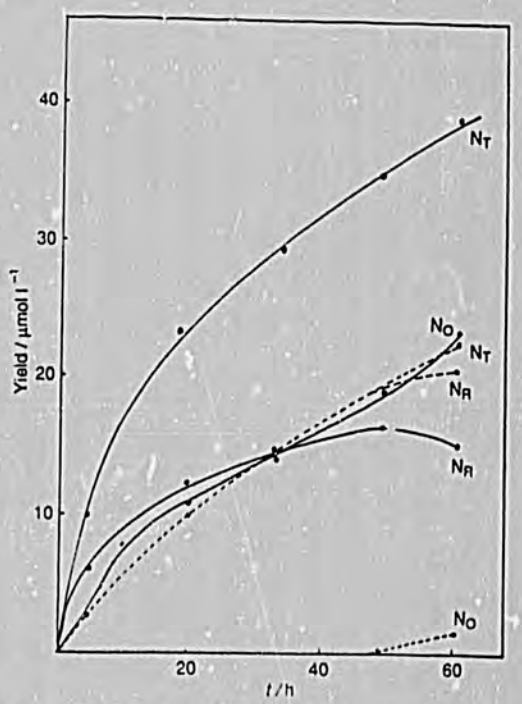

Fig. 2 Yields of reduced (N_R), oxidised (N_O) and total (N_T) nitrogen in irradiation of the loaded Nafion film at pH 12.0 in (——) air purged (- - -) N_2 purged solutions. (pH = 12.0)

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The general belief is that NP semiconductor dispersions photoproduce [illegible] (2) [illegible] could also be transferred to chemisorbed N_2, as in reaction (3)

$$N_2 + 6H^+ + 6e^- \text{ (conduction band)} \rightarrow 2NH_3 \quad (1)$$

$$2H_2O + 4h^+ \text{ (valence band)} \rightarrow O_2 + 4H^+ \quad (2)$$

$$N_2 + 4H_2O + 6h^+ \rightarrow 2NO_2^- + 8H^+ \quad (3)$$

$$2H_2O + N_2 + O_2 + 2h^+ \rightarrow 4H^+ + 2NO_2^- \quad (4)$$

In addition to the activation barrier, reaction (3) necessitates transfer of six holes compared to four in the case of reaction (2). Thus, reaction (3) cannot happen to an appreciable extent [small quantities of N_O seen in NP systems[5-7] probably originate from photooxidation of NH_3 by O_2 from reaction (2)]. In the presence of O_2, another hole-consuming process is possible [see reaction (4)]. The reaction between chemisorbed N_2 and O_2 is more probable as it involves transfer of two holes compared to six in the case of reaction (3). Again the hole-transfer to OH^- leading to reaction (2) is suppressed as the cation exchange membrane cannot easily accommodate OH^- ions. We believe that reactions (1) and (4) are responsible for the photosynthesis of N_R and N_O in the AP Nafion–hydrous iron(III) oxide system. As O_2 readily accepts electrons to form $O_2^{\cdot-}$, which in turn scavenges holes, the reactions (1) and (4) occur more effectively when electron donation to O_2 is suppressed. Presumably, the microenvironment of the Nafion matrix[8] is suppressing the formation of $O_2^{\cdot-}$. Hydrated iron(III) oxide-loaded Nafion films remained active for nearly 60 h of irradiation. However, on repeated use, some deterioration which affects N_T as well as the relative proportions of N_R and N_O is noted. The optimum pH for both N_R and N_O yields is *ca.* 12.0. At neutral pH they are reduced [illegible] kinetically favourable [illegible] the reaction (1), the flat-band potential of hydrous iron(III) oxide shifts in an unfavourable direction with the decrease of pH.[9] The two opposing effects leads to an optimum pH. Furthermore, with progress of the reaction, pH decreases resulting in a gradual decline of the rate of production of N_R (Fig. 1). The molar ratio $NO_2^- : NO_3^-$ depends on the pH and the rate of purging.

Reactions (1)–(4) indicate the possible overall stoichiometry in fixation of N_2. As multi-electron transfer is highly improbable the above reactions could involve several primary steps.

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PHOTOINDUCED OXIDATIVE NITROGEN FIXATION REACTIONS ON SEMICONDUCTOR SUSPENSIONS

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An aqueous suspension of ruthenium doped TiO_2 photocatalyses the conversion of molecular nitrogen to ammonia and nitrate under irradiation with UV light. In comparison, the TiO_2 catalysts coated with the metals silver, mercury and platinum appear to produce predominantly ammonia while ZnO produces only nitrate. In these photo-oxidations molecular nitrogen is initially reduced to NH_3 which then undergoes further reaction with photogenerated hydroxyl free radicals to yield nitrate.

1. Introduction

Photofixation of dinitrogen on irradiated semiconductor surfaces is an attractive way of solar energy conversion [1]. Several TiO_2-based catalysts produce ammonia upon irradiation with UV light in a stream of N_2. Solids [2], wafers [3] and aqueous suspensions [4] have been employed. The yields in all cases are small (10^{-6} mol range) and the activity decreases with time [4]. Compared to photoreduction of N_2 to NH_3, there is little work reported on oxidative nitrogen fixation reactions on irradiated semiconductor surfaces. Bickley has reported [5] the photo-oxidation of N_2 to NO on UV irradiated rutile while Schrauzer has observed the photo-oxidation of the initially formed NH_3 to NO_2^- on Fe-doped TiO_2 [1]. On account of the reported [6] photo-oxidation of NH_3 on TiO_2 it is conceivable that the decreasing yields in most of these reactions is due to photo-oxidation of NH_3. Photoreduction of N_2 to NH_3 on Ru-doped rutile has been reported [7]. With the latter system, however, we find that NO_3^- is observed in higher yields than NH_3. On the other hand TiO_2 powders coated with Ag, Hg or Pt are poor oxidation catalysts while exhibiting moderately high activity for the photosynthesis of NH_3. With ZnO, however, the only photoproduct is NO_3^-.

2. Experimental

2.1. Preparation of catalysts

Ru-doped TiO_2 catalyst was prepared by mixing TiO_2 powder (99.99%, Aldrich) with $RuCl_3 \cdot 3H_2O$ (so that the final product contains ~ 0.2% RuO_2) in aqueous

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solution. The resultant slurry was first evaporated to dryness and then heated at 1000°C for 2 h in air. The metal-coated powders were prepared by mixing the appropriate metal salt solutions of Pt, Hg and Ag with TiO_2 in the presence of a reducing agent such as citric acid followed by irradiation of the suspensions under a UV lamp for 4 h. ZnO was prepared by heating freshly prepared $Zn(OH)_2$ at 300°C for 2 h. All catalysts and reagents were carefully purified to remove any traces of NH_3 and NO_3^- by warming with Al/NaOH followed by repeated washing with deionized water. X-ray powder diffraction spectra were obtained using Cu Kα radiation on a Shimadzu model XD-7A diffractometer.

2.2. Procedure

0.200 g of the powdered catalyst was suspended in 300 ml of double distilled water and irradiated with stirring using a 400 W medium pressure mercury lamp in an immersion well type photochemical reactor (Applied Photophysics). This lamp produces $> 5 \times 10^{19}$ photons/s inside the reaction flask. A slow stream of N_2, purified by passing through a heated copper pellet column, chromic acid solution, NaOH solution and water was passed through the reactor. Control experiments were carried out under argon and in the dark. At the end of irradiation, 10 ml of 0.10M NaOH was added to the reaction flask and the contents were distilled into a receiving flask, containing 10 ml of 0.10M HCl. The ammonia thus absorbed was determined by the indophenol blue method [8]. This method is accurate to determine NH_3 concentrations in the 1–50 μmol ℓ^{-1} range. The nitrate present in solution was determined by taking 10 ml of the solution after centrifugation to remove the catalyst, followed by a Cd reduction and colorimetric determination with sulfanilamide coupled with N-(1-naphthyl) ethylenediamine dihydrochloride.

3. Results and discussion

The experimental results are shown in figs. 1 and 2. The yields are in the μmol range and comparable to those reported by other workers. Ru-doped TiO_2 is the most active catalyst for N_2 fixation with higher NO_3^- yields than NH_3. Another noteworthy observation is that the catalytic activity does not decrease at least up to 24 h of irradiation. After 24 h, there was a gradual loss of activity arising probably from back-reactions as well as due to blocked catalytic sites from irreversible adsorption of NH_3 and/or NO_3^-. The total nitrogen fixed (3 μmol after 8 h) is higher than the yield of NH_3 reported for catalytic systems such as $RuO_2 \cdot NiO \cdot BaTiO_3$. The quantum yield for this reaction is ~0.02%. The metal-coated TiO_2 catalysts on the other hand are moderately active for NH_3 synthesis while yielding only smaller amounts of NO_3^-. With ZnO, however only NO_3^- is produced under identical experimental conditions. Control experiments carried out under argon and in the dark produced no detectable traces of NH_3 (< 0.1 μmol) or NO_3^- (< 0.01 μmol). In order to establish that the NH_3 and NO_3^- arose from the photochemical reaction of the catalyst with N_2(g), the catalyst was recycled a few times. Results

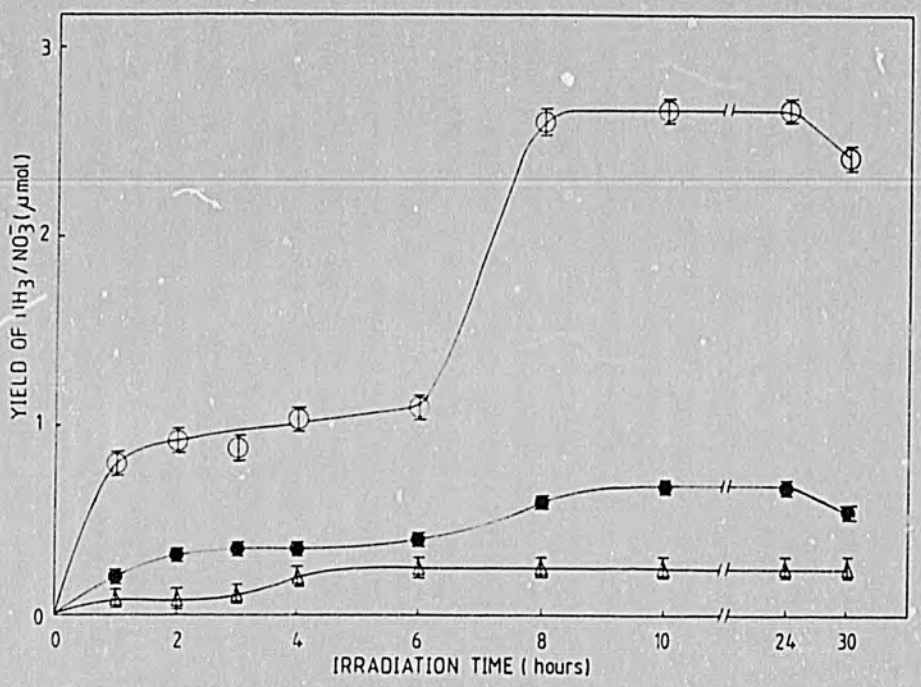

Fig. 1. Yields of NH_3/NO_3^- for RuO_2/TiO_2: (○) NO_3^-, (●) NH_3; and for ZnO: (△) NO_3^-.

obtained for the same duration of irradiation were identical within experimental error. This establishes the fact that any photochemical reactions with a thermally prefixed nitrogen moiety formed during the calcination stage to give NH_3 are insignificant under our experimental conditions.

When semiconductors such as TiO_2 are used as photocatalysts, under irradiation, electron–hole pairs are generated on the semiconductor surface:

$$TiO_2 \xrightarrow{h\nu} TiO_2^* \ (h^+, e^-). \tag{1}$$

The excited electrons are used for the photoreduction of H_2O to H_2,

$$2\,H_2O + 2\,e^- \rightarrow H_2 + 2\,OH^-, \tag{2}$$

which in turn is utilized for NH_3 synthesis.

A mechanism involving direct reduction of N_2 to diazene which eventually disproportionates to NH_3 has also been suggested [1]. The photogenerated holes could oxidize water to oxygen and also oxidize any adsorbed OH^- to OH free radicals [9]:

$$4\,h^+ + 2\,H_2O \rightarrow O_2 + 4\,H^+, \tag{3}$$

$$h^+ + OH^- \rightarrow OH^{\cdot}. \tag{4}$$

The photogenerated OH free radicals could bring about the oxidation of NH_3 and could explain the decreasing ammonia yields with a concomittant increase in NO_3^-

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catalytic activity was found to be ~0.2% (as RuO_2). Such catalysts have greater catalytic activity in terms of the total nitrogen fixed compared to physically mixed powders. The activity of metal-coated TiO_2 catalysts can be attributed to the enhanced H_2 evolution of these surfaces. However, the NH_3 yields differ only slightly for the metals, Pt, Ag and Hg. Furthermore, as hole transfer catalysts these metals are inferior to RuO_2 and hence the higher yields of NO_3^- obtained with Ru doped TiO_2 can be explained.

The most significant finding from these studies is the eventual photo-oxidation of the N_2 molecule to the more stable NO_3^- via NH_3. Compared to direct oxidation of NH_3 by O_2, a pathway involving the reaction of NH_3 with OH free radicals or peroxide is more favourable. Thus we find no significant variation in the yields of NH_3 and NO_3^- when irradiations were carried out in air instead of N_2. The formation of adsorbed H_2O_2 on TiO_2 surfaces is now established [11]. It is now generally believed that the dimerization of the OH free radicals formed during the capture of surface OH^- by the photogenerated holes gives rise to adsorbed H_2O_2. The formation of OH free radicals has been proposed [12] in some hydroxylation reactions of organic substrates induced by near UV photolysis of aqueous TiO_2 suspensions. From the available evidence we propose that the NH_3 first undergoes [13] oxidation by OH free radicals to give NO_2^- which in turn gets further oxidized by H_2O_2 to NO_3^-. Although in our experiments traces of NO_2^- could be detected during long time irradiations (> 12 h), NO_3^- is the predominant product. With ZnO suspensions, the only product obtained is NO_3^- with no detectable amounts of NH_3 (< 0.1 μmol). It has been shown that irradiation of ZnO suspensions produces O_2^- under UV illumination [9]. The superoxide could disproportionate to O_2^{2-} and along with the OH free radicals would lead to NO_3^- as the final product.

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Photocatalytic Behaviour of Metal doped Titanium Dioxide

Studies on the Photochemical Synthesis of Ammonia on Mg/TiO_2 Catalyst Systems

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ABSTRACT

Magnesium doped titanium dioxide was found to convert nitrogen to ammonia upon UV irradiation. The effects of magnesium dopant level, calcination temperature, duration of heating of the catalyst and pH affect the ammonia yield. The optimum conditions were 2–4% magnesium doping level and heating of the catalyst at 500°C for 2 h.

Keywords: magnesium/titania, ammonia synthesis, photocatalysis, catalyst preparation (metal doping)

INTRODUCTION

Metal ion doping of TiO_2 has been investigated as a possible way to improve the efficiency of TiO_2 catalysts for the photosplitting of water [1] and also for the photoreduction of nitrogen to ammonia [2]. Doping with a metal ion of different valence is known to alter the catalytic properties of a semiconductor

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[3]. This can also improve the adsorption properties of the catalyst and extend the absorption of light to the visible region. In our efforts to optimize the photoreduction of nitrogen to ammonia on semiconductor surfaces, we have studied the Mg^{2+}–TiO_2 system which exhibits enhanced photocatalytic effects compared to TiO_2 alone [4]. The efficiency of this catalyst was found to depend on the level of Mg^{2+} doping, mixing temperature and the duration of heating of the sample.

EXPERIMENTAL

Preparation of the catalyst

TiO_2 powder (BDH) was first suspended in distilled water and the calculated amount of $MgSO_4 \cdot 7H_2O$ (AR grade) was added. After stirring for 24 h, the mixture was evaporated to dryness and the samples for this study were obtained by heating at different temperatures for varying periods of time in air. The catalysts so obtained were characterized by X-ray powder diffraction on a Shimadzu XD7A powder diffractometer. Particle size analyses were carried out on a Horiba particle size analyzer using the sedimentation technique.

Irradiation procedure

All irradiations were carried out using a 400 W medium pressure Hg arc lamp. The lamp is housed in an immersion well type quartz reactor with an inner water cooled jacket. The lamp produces $> 5 \times 10^{19}$ photons/s/cm^2. An amount of 0.200 g of the catalyst suspended in 300 ml of double distilled water was irradiated under a slow stream of purified nitrogen. Control experiments were carried out under argon and in the dark. After the irradiation, the contents were treated with 10 ml of 0.10 *M* NaOH and the ammonia distilled off to a receiving flask containing 10 ml of 0.10 *M* hydrochloric acid. The ammonia in the distillate was determined by the indophenol blue method.

RESULTS AND DISCUSSION

Fig. 1 shows the effect of different Mg^{2+} doping levels on the yields of ammonia and NO_3^- obtained. The optimum yields are obtained after ca. 2 h of irradiation. The ammonia yields after 2 h were highest for a Mg^{2+} dopant level of 2–4%. A similar effect was observed by Kiwi and Graetzel [4] for hydrogen generation over Mg^{2+} doped TiO_2 catalysts. At higher levels of magnesium doping, we observed that the Mg^{2+} initially added is not wholly incorporated into the TiO_2 structure as seen from the determination of Mg^{2+} in the actual catalyst samples using atomic absorption spectrometry. X-ray powder diffraction patterns of the catalyst doped up to 8% did not exhibit any evidence of

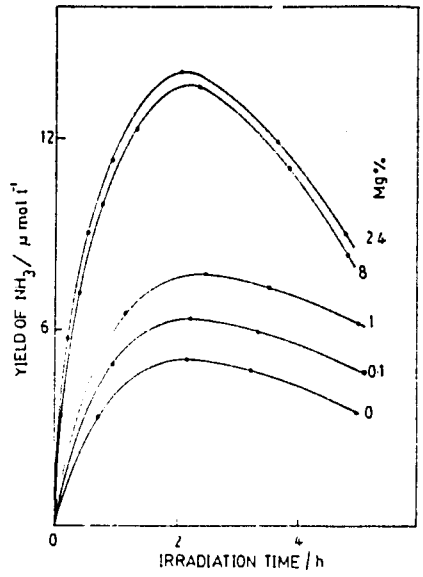

Fig. 1. Variation of the ammonia yields with time at different magnesium dopant levels (doping temperature 500 °C, doping time 2 h).

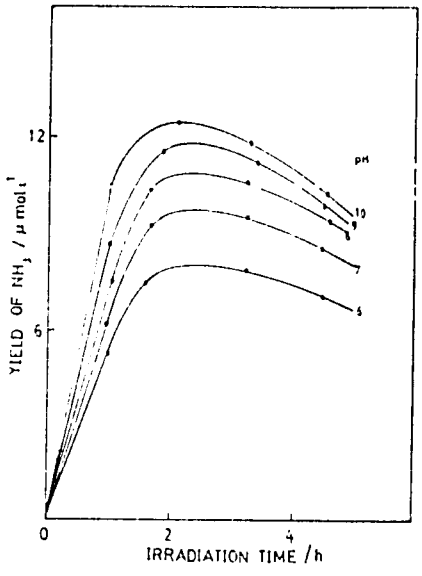

Fig. 2. Variation of the ammonia yield with time at different pH values (doping temperature 500 °C, dopant level 2%, doping time, 2 h).

titanate formation. Particle size analysis on the catalyst with optimal activity (2% dopant level, heated at 500°C for 2 h) showed that the average particle diameter is 0.64 μm compared to undoped TiO_2 (0.57 μm). The respective surface areas are 2.384 $m^2 g^{-1}$ (Mg/TiO_2) and 2.622 $m^2 g^{-1}$ for undoped TiO_2.

The effect of pH on this reaction was also studied. The results (Fig. 2) show that the yields of ammonia increase with increase in pH. At higher pH values more NO_3^- is also produced. The optimum temperature and the duration of heating was found to be 500°C and 2 h respectively (Figs. 3 and 4). Higher temperatures and higher periods of heating cause titanate formation and hence decreased activity. Furthermore the diffusion of Mg^{2+} into the TiO_2 lattice appears to be detrimental to its catalytic activity.

TiO_2 can accommodate massive defect levels especially at the surface. The alteration of catalytic properties in a semiconductor by doping catalysts with ions of different valency was first observed by Verwey et al. [3]. Thus Li^+ and Mg^{2+} doping of TiO_2 leads to enhanced water photocleavage under UV irradiation [4,5]. Doping with Mg^{2+} creates a narrower depletion layer width, which affects the rate of band bending. This would allow electron tunneling to proceed more easily at the interphase, thereby enhancing electron transfer. This hypothesis could explain the enhanced yields of ammonia observed in the above system. Our yields are significantly higher than those observed by Schrauzer and Guth [2] with other metal doped TiO_2 catalysts fired at 1000°C.

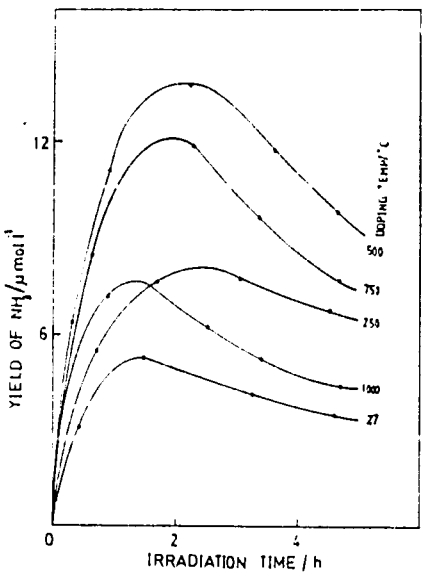

Fig. 3. Variation of the ammonia yield with time at different catalyst doping temperatures (dopant level 2% pH = 10, doping time 2 h).

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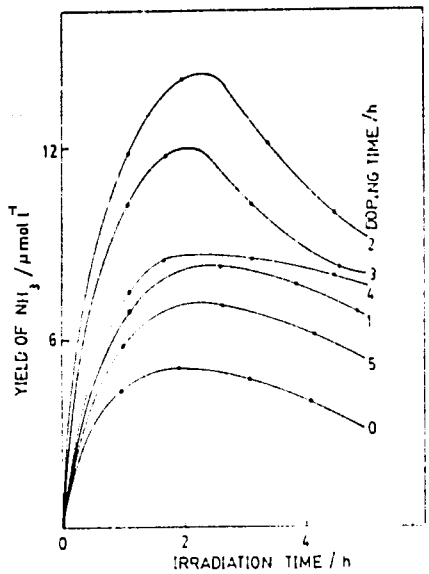

Fig. 4. Variation of the ammonia yield with time at different doping times (dopant level 2%, pH = 10, doping temperature 500 °C).

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PHOTOREDUCTION OF N_2 TO NH_3
&
H_2O TO H_2 ON METAL DOPED TiO_2 CATALYSTS (M=Ce,V)

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A B S T R A C T

The photosynthesis of NH_3 from N_2 and the photogeneration of H_2 from H_2O under non-sacrificial conditions on M/TiO_2 (M = Ce, V) are reported. The yields are superior to those earlier reported for similar metal doped TiO_2 catalysts. The flat band potentials of these catalysts have been determined and correlated to their catalytic activity.

INTRODUCTION

Metal doped TiO_2 catalysts have been widely investigated for the photosplitting of water and also for several other reactions in organic and inorganic conversions . Some of these include the photoreduction of N_2, [1-5] CO_2 [6-8] metal ions, [9-10] organic conversions [11] and for generating H_2 from organic wastes [12]. Metal ions doped into the TiO_2 lattice create defects in the rutile structure resulting in modified adsorption properties of the substrate [13]. Metal ion doping also shifts the absorption spectrum of the undoped semiconductor more into the visible region[14]. Sometimes, free metals such as Pt,Pd and Hg are deposited on the semiconductor particles to improve photocatalytic effeciency[15]. In this case, such metal islands rapidly conduct away the photogenerated electrons and hence act as electron reserviors for photoredox reactions.

Several investigations on the use of metal doped TiO_2 catalysts have been reported [1-5]. The role of the metal ions in the catalyst is poorly understood. We have reported [16] that in the case of Mg/TiO_2 catalysts, the conditions in the preparation of the catalyst determine the degree of photocatalytic activity. Transfer of photogenerated electrons to the metal ions followed by its reduction may also be an important factor in determining photocatalytic activity. The present investigation reports the photoreduction of N_2 and H_2O on M/TiO_2 (M = Ce,V) and the variables in the preparation of the catalyst which affect such catalytic activity.

EXPERIMENTAL

Preparation of catalysts:

All reagents used were AR grade and further purified to remove all traces of NH_4^+, NO_2^- and NO_3^- by warming with Al/NaOH. Metal doped TiO_2 were prepared by mixing TiO_2 powder (Aldrich, 99.99%, anatase) with purified ceric sulphate or vanadyl sulphate in aqueous solution. The resultant slurries were first evaporated to dryness and the solids obtained were next calcined at the following temperatures for varying periods of time in air using a muffle furnance: 250°C, 500°C, 750°C and 1000°C.

A A sample dried at room temperature was also used for subsequent irradiations. Other variables investigated in the catalyst preparation were, the percentage of metal doped, heating time and pH.

Characterisation of the Catalysts

X-ray powder diffraction measurements were carried on a Shimadzu XD-7A model diffractometer with CuK α radiation. The reflectance spectra of the samples were obtained using the full integration sphere of a Shimadzu model 365 UV-VIS spectrophotometer. Particle size analyses were carried out on a Horiba model CAPA-700 particle size analyzer using the sedimentation technique. Differential thermal analysis measurements were performed on a Shimadzu model DT 40 DTA analyzer.

Irradiation Procedure

M/TiO_2 catalysts (M=Ce,V) prepared under different conditions (calcination temperature, heating time and the percentage of metal doped) were suspended in 250 ml of distilled water in an immersion well type photochemical reactor (Applied Photophysics, UK). The water was freshly distilled form an all glass still. For each run 0.200g of the composite catalyst was used. Irradiations were carried out using a 400W medium pressure mercury lamp housed inside a water cooled quartz jacket. The lamp emits $>7 \times 10^{19}$ photonsS^{-1} inside the reaction flask. A slow stream of N_2, purified by passing through a heated copper pellet column, chromic acid solution, NaCH solution, and H_2O was passed through the reactor.

Effluent gases from the reactor were bubbled through a trap containing 10ml of 0.1 M HCl. The suspension in the reactor was magnetically stirred throughout the irradiation. Control experiments were carried out under N_2 in the dark and also under irradiation with argon.

After irradiation, the mixture in the reactor flask was treated with 10 ml of 0.2M NaCH and the ammonia in solution was distilled into the trap containing 10ml of 0.1M HCl. The ammonia in the distillate was determined colorimetrically by the indophenol blue method [17].

The nitrate content of the solution was determined colorimetrically by the coupling reaction of sulphamide with N-(1-naphthyl) ethylene diamine dihydrochloride after cadmium reduction.

Hydrogen Evolution Experiments

Hydrogen evolution during photolysis under both N_2 and argon was determined by gas chromatography (Shimadzu GC-9AM gas chromatrgraph, molecular sieve column and carrier gas argon). These results were independently checked by carrying out photolysis in a reaction vessel provided with a polarographic detector (Applied Photophysics).

Determination of Flat-band Potentials

Pellets prepared from catalyst powders (diameter 13.0 mm, thickness 1.80 mm) compacted to a pressure of 40 MPa were used to measure electrical conductivity. Mott-Schottky plots at frequencies 500Hz and 1kHz were obtained on these pellets using a Hewlett - Packard LCR meter model 4192 A and a Kenwood DL-707 Digital multimeter.

RESULTS & DISCUSSION

Photoreduction of N_2

In order to optimize N_2 reduction with respect of the conditions of the catalyst preparation, the effects of the following variables on the yield of NH_3 were studied; percentage doping, heating temperature, heating time and pH. (Figures 1 -4). The optimal conditions obtianed form these studies for the Ce/TiO_2 system were: dopant concentration of 10% (w/w), heating temperature of 250°C, heating time of 3h and a pH of 12.5. The corresponding values for the V/TiO_2 catalyst were : dopant concentration of 10% (w/w), heating temperature 750°C, heating time 4h and a pH of 3. With the latter system, at higher pH values, vanadium ions leach into solution. The time variations of NH_3 obtained for catalysts prepared under optimal conditions are given in Figure 5. The maximum yield of NH_3 in solution obtained for Ce/TiO_2 is ca. 30 $\mu mol\ l^{-}$ while for the V/TiO_2 system it is ca. 28 $\mu mol\ l^{-}$. Both these values are considerably higher than those

reported by others for metal doped TiO_2 catalysts [1].

X-ray powder diffraction patterns and FT-IR spectra obtained on Ce/TiO_2 samples showed that sulphate ions are present in the catalyst used. The enhancement of N_2 reduction in similarly constituted catalysts has been observed by Xiao et.al [18] and attributed to the enhanced adsorption of N_2 on the catalysts. Particle size distribution for the Ce/TiO_2 catalyst prepared under optimal conditions shows that the average particle size is 0.9 μm corresponding to a surface area of 1.54 $m^2\ g^{-1}$.

With the V/TiO_2 catalyst where the optimum doping temperature is 750°C, the TiO_2 is present predominantly in the anatase form. The average particle size is 1.5 μm corresponding to a surface area of 3.4 $m^2\ g^{-1}$. The time development of NH_3 showed an unusual periodic variation when compared to the Ce/TiO_2 catalyst. In both cases, the reduction in NH_3 yields was folowed by a concomittant slow increase in nitrate formation owing to the photooxidation of ammonia.

Photogeneration of H_2

Both catalysts yield H_2 upon irradiation in aqueous solution. Irradiations carried out with Ce/TiO_2 under both argon and N_2 indicate a steady increase in H_2 generation under non-sacrificial conditions. Nearly 1000 μl of H_2 are produced after 24 hours [figure 6]. The yields of H_2 under N_2 and argon are not significantly different suggesting that "nitrogen assisted hydrogen evolution" [19] does not occur with this catalyst system. The yield of H_2 with V/TiO_2 under sacrificial conditions in the presence of ethanol are considerably enhanced. [figure 6].

Flat band potentials

The Mott-Schottky plots for Ce/TiO_2 and V/TiO_2 pellets in aqueous solution (pH = 12,3) at frequencies 500 Hz and 1 kHz are presented in figures 7 & 8. Table 1 gives the results on the positions of the E_{CB} and E_{VB} calculated from the flat-band potential values and the band gaps determined from reflectance measurements. The carrier densities, n_D were calculated from the slopes of the Mott-Schottky plots using the formula,

$n_D=(2/\ \varepsilon\varepsilon_o\ \ e\ A^2)1/m$ where ε_o is the permittivity of vacuum, ε is the dielectric constant of the semiconductor, e is the electronic charge, A is the area of the elctrode and m is the slope of the graph. The results on V/TiO_2 catalysts confirm its n-type behaviour with a E_{CB} value of -2.8V at pH 3 (vs SCE) while for the Ce/TiO_2 system the corresponding value is -2.1 V(vs SCE), at pH 12. The corresponding value for TiO_2 (anatase) is -1.2V (vs SCE). The consistently higher hydrogen evolution rates from V/TiO_2 catalyst when compared to Ce/TiO_2 catalyst (Figures 7 & 8) is consistent with the above data. However the NH_3 yields do not vary significantly between the two catalysts.

Acknowledgement:

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FIGURE AND TABLE CAPTIONS

Figure 1. The variation of NH_3 yield with dopant amount (a) Ce/TiO_2 (b) V/TiO_2.

Figure 2. The variation of NH_3 yield with heating temperature (a) Ce/TiO_2 (b) V/TiO_2.

Figure 3. The variation of NH_3 yield with heating time (a) Ce/TiO_2 (b) V/TiO_2.

Figure 4. The variation of NH_3 yield with pH. (a) Ce/TiO_2 (b) V/TiO_2.

Figure 5. The variation of NH_3/NO_3^- yields with irradiation time a - NH_3 yield for Ce/TiO_2 b - NH_3 yield for V/TiO_2, a' - NO_3^- yield for Ce/TiO_2 b' - NO_3^- yield for V/TiO_2.

Figure 6. The variation of H_2 yield with irradiation time. a - Ce/TiO_2 under argon, a' - Ce/TiO_2 under N_2 b - V/TiO_2 under argon, b' - V/TiO_2 under N_2.

Figure 7. Mott-Schottky ($1/C^2$ Vs V) plot for Ce/TiO_2.

Figure 8. Mott-Schottky ($1/C^2$ Vs V) plot for V/TiO_2.

Table 1. Band gaps and Band positions of composite catalysts, M/TiO_2 (M=v; Ce)

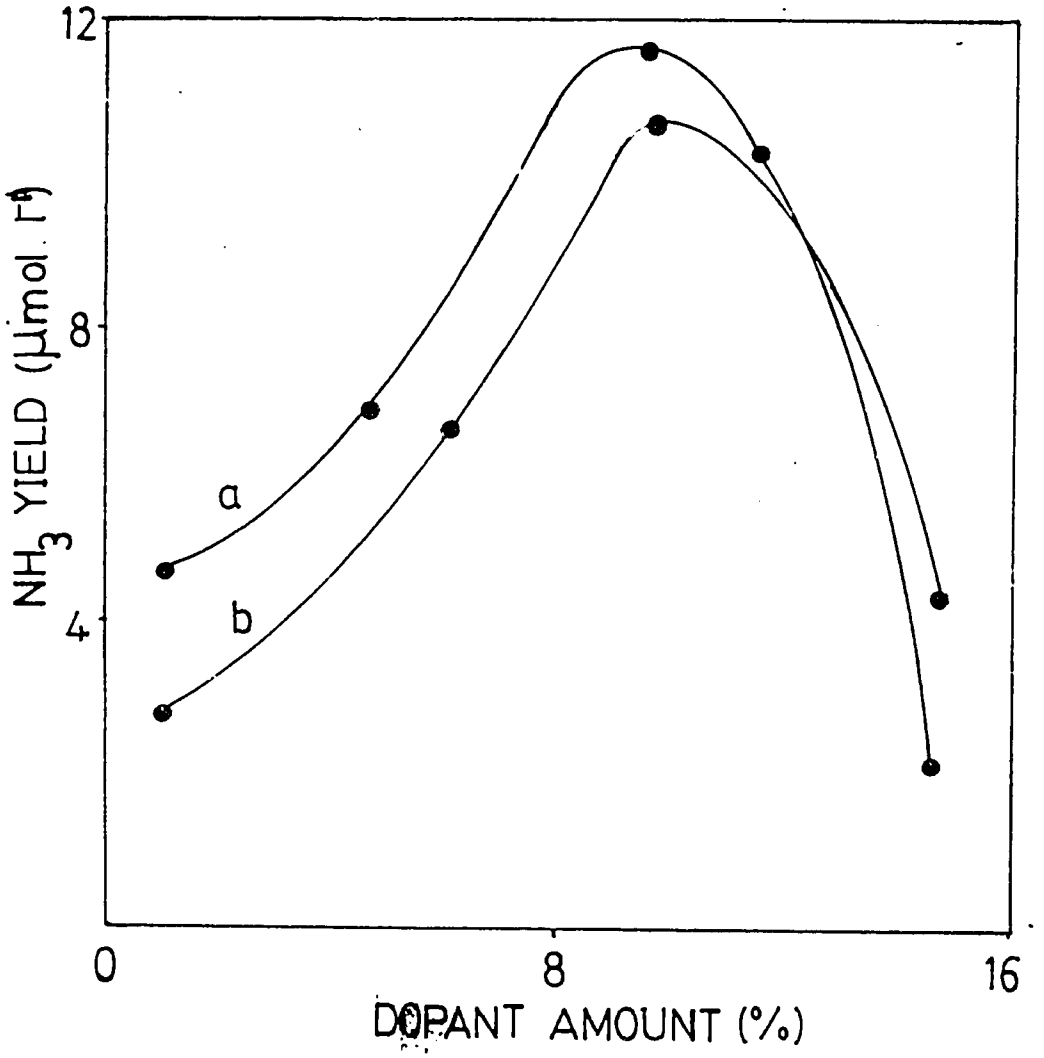

Fig. 1

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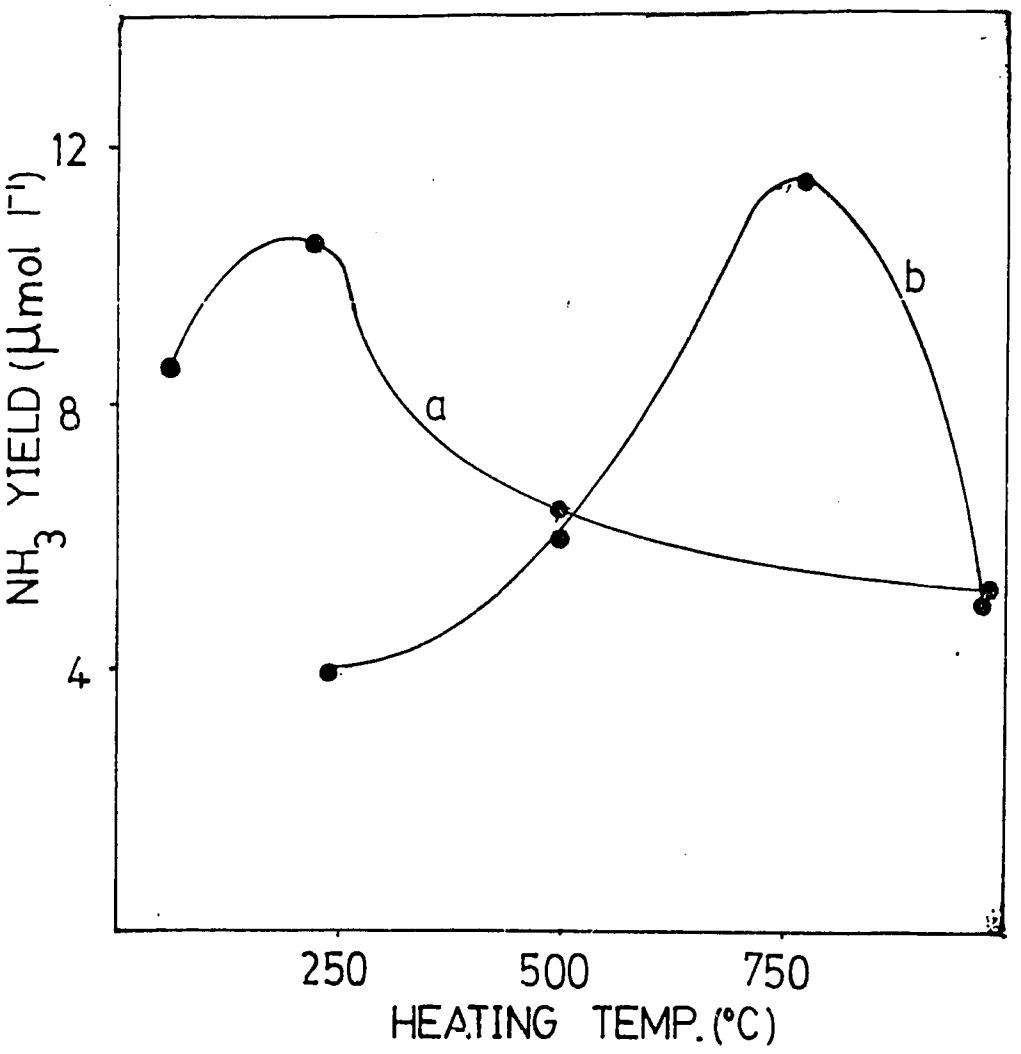

Fig. 2

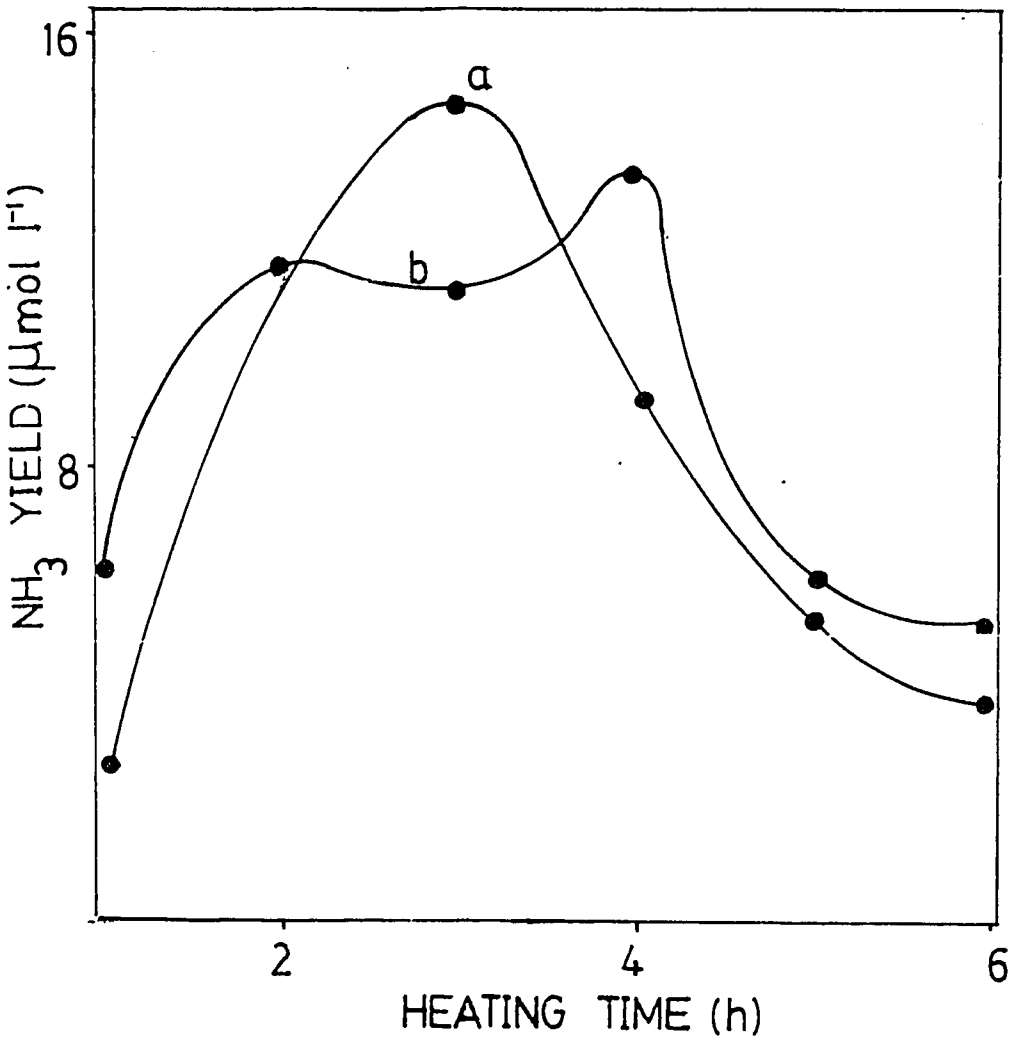

Fig. 3

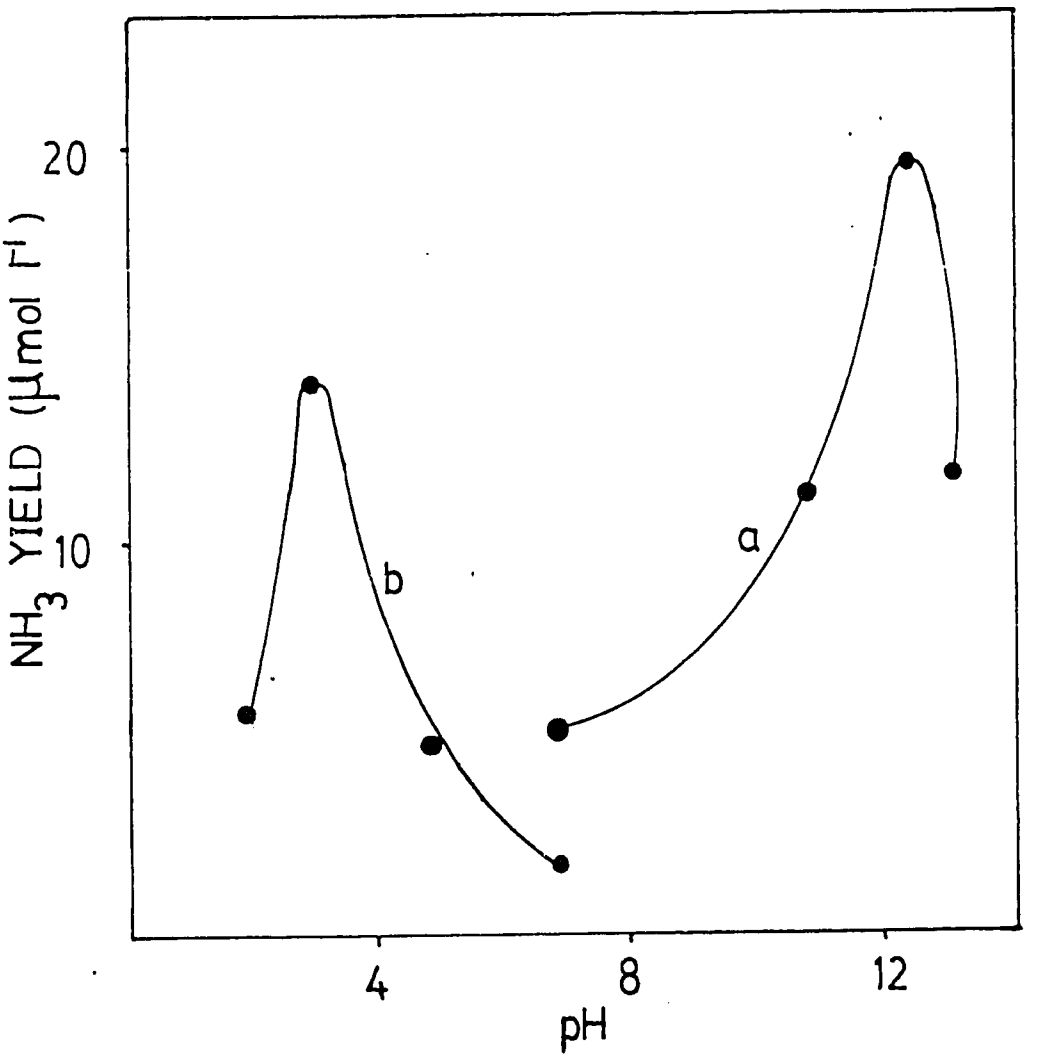

Fig. 4

TABLE 1

Band gaps and Band positions of composite catalysts, M/TiO_2 (M=V,Ce)

Catalyst	Type of the[a] Semiconductor	pH	E_{FB}(vs SCE)[b]	E_{BG}(eV)[c]	E_{VB}(vs SCE)	E_{CB}(vs SCE)	$N_D(cm^{-3})$[d]
V/TiO_2	n	03	-2.8	3.2	+0.4	-2.8	$4\sim6 \times 10^{21}$
Ce/TiO_2	p	12	+1.1	3.1	+1.1	-2.0	$1\sim2 \times 10^{20}$

a From the sign of the Mott-Schottky plot slopes

b From Mott-Schottky plots cf. experimental section

c From reflectance data

d N_D, doping concentration determined from $n_D=(2/\varepsilon\varepsilon_o eA^2)1/m$

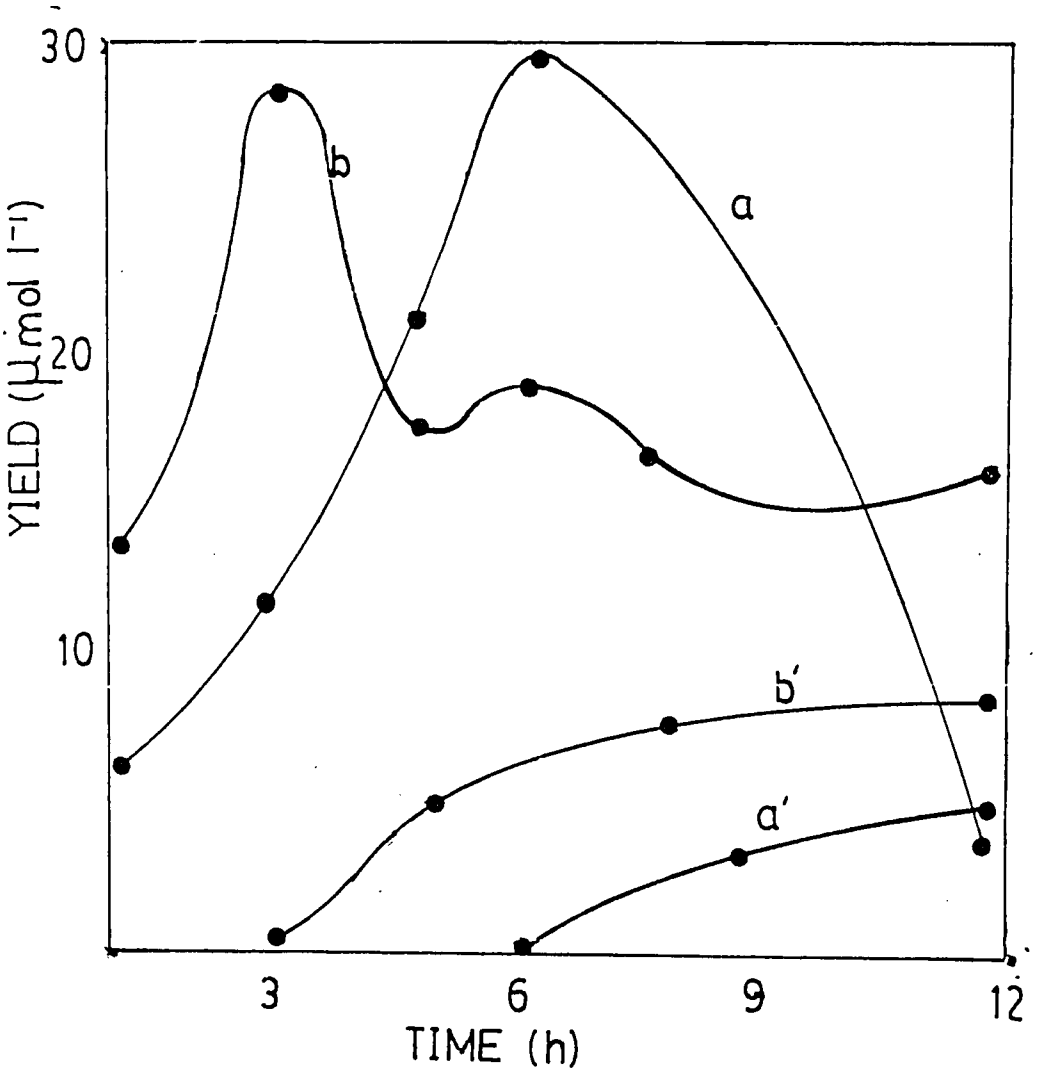

Fig. 5

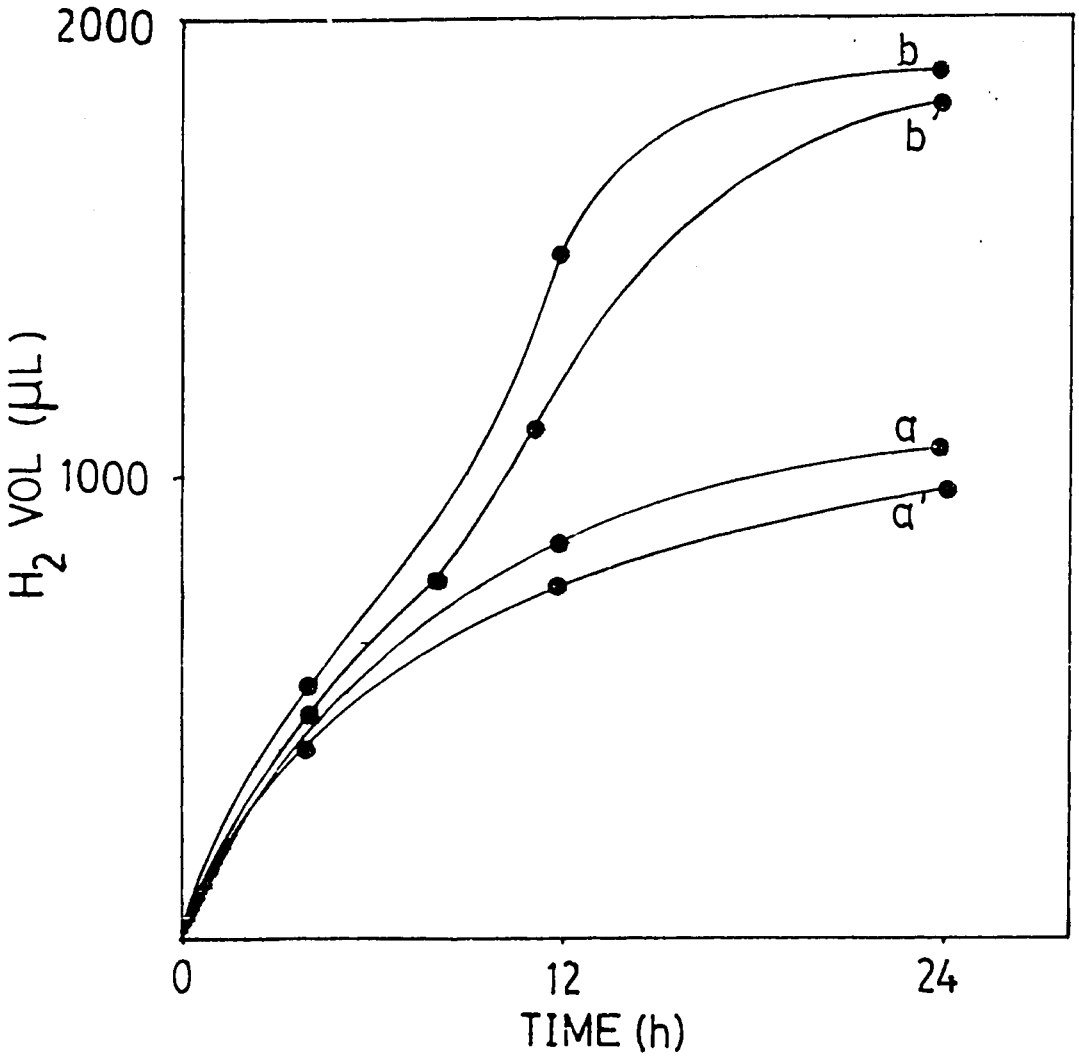

Fig. 6

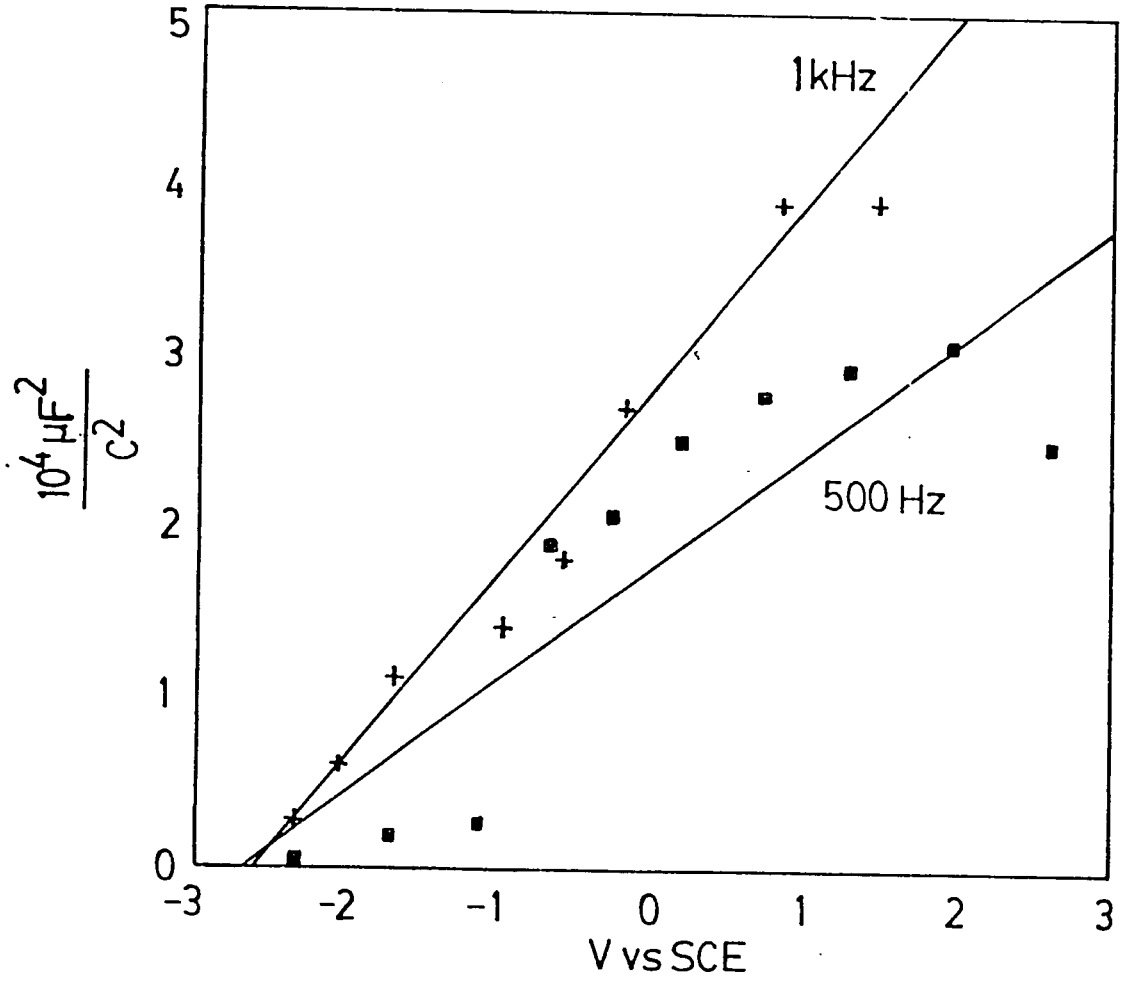

Fig. 8

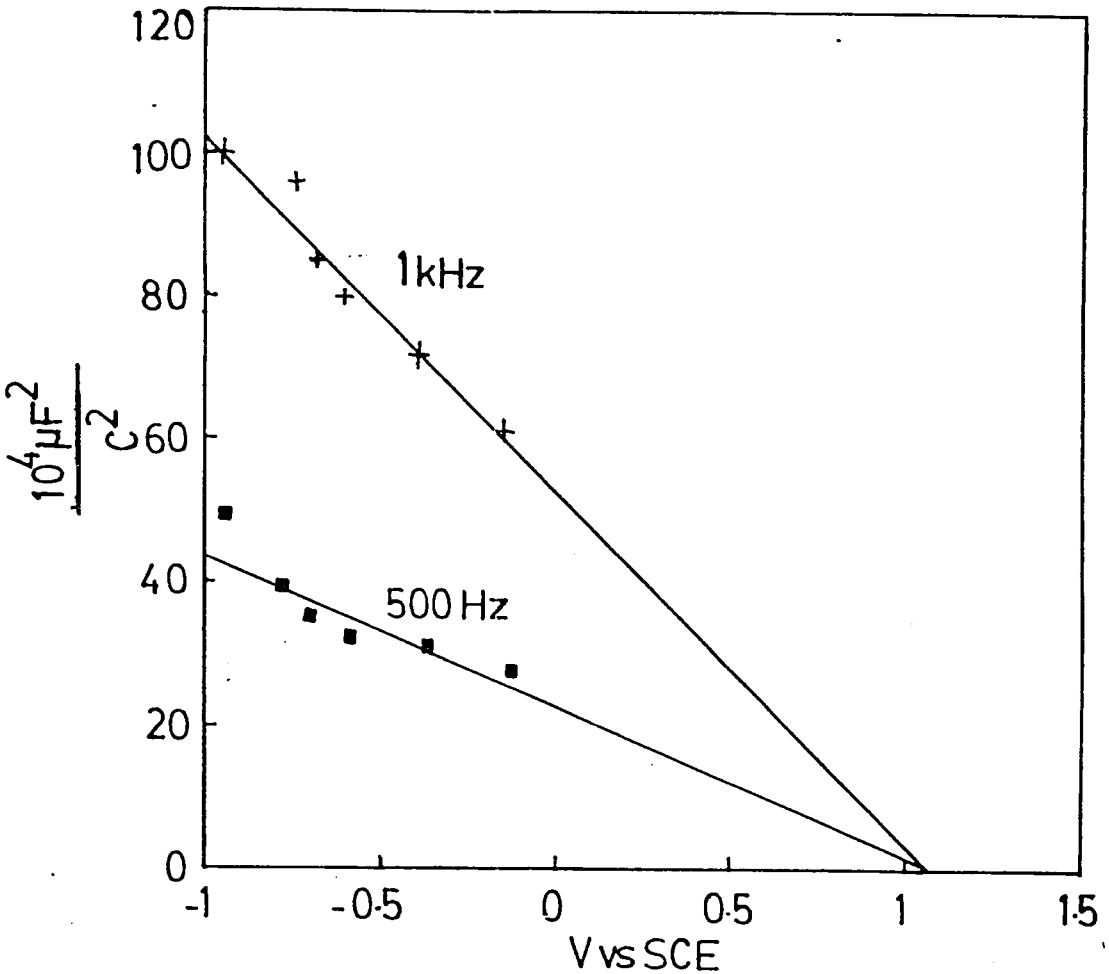
120
100
80
60
40
20
0
$\frac{10^4 \mu F^2}{C^2}$
1kHz
500 Hz
-1
-0.5
0
0.5
1
1.5
V vs SCE

Fig. 7

PHOTOINDUCED REDUCTION OF WO_3 BY TiO_2 AND ITS ROLE ON PHOTOCHEMICAL SYNTHESIS OF NH_3

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Abstract

Irradiated TiO_2 reduces WO_3 to blue $WO_{2.96}$. The reduced tungsten species converts N_2 to NH_3 both in the gas phase and in aqueous suspensions. Some NH_3 formed is photooxidized to NO_3^- in aqueous suspensions while there is relatively little oxidation at the gas/solid interphase. Irradiation over longer periods results in bronze formation and loss of photocatalytic activity.

Introduction

Photosynthesis of NH_3 on irradiated semiconductors either in the gas phase or in aqueous suspensions have been investigated as a possible way of solar energy conversion to give a useful product[1-4]. Some of the systems that have been studied include metal doped TiO_2[5], hydrous Fe_2O_3[6] and substoichiometric forms of WO_3[7]. The quantum yields in all cases are small and in general back reactions result in rapid loss of catalytic activity with time.

It has been shown[7] that the reaction of moist N_2 on blue tungsten oxides in the solid phase containing $WO_{2.96}$ gives NH_3. This reaction is enhanced by irradiation. However aqueous suspensions of WO_{3-x} powder reduced N_2 to NH_3 via only a thermochemical path. The participation of reduced tungsten centers in chemically reducing N_2 to NH_3 has been suggested for the above reaction (Eq.1)

$$WO_{2.96} + 0.04H_2O + (0.04/3)N_2 \longrightarrow WO_3 + (0.08/3)NH_3 \quad (1)$$

We have observed that irradiated TiO_2 is capable of reducing the yellow form of tungsten oxide, WO_3, to a blue reduced form. This observation suggests the possibility of developing a cyclic pathway for the photosynthesis of NH_3 based on the composite system WO_3/TiO_2 and the results are reported here.

Experimental

Catalyst preparation

All reagents used were AR grade and further purified chemically to remove all traces of ammonia and nitrate. An aqueous suspension of TiO_2 (Aldrich, anatase) was treated

with a Na_2WO_4 solution and carefully acidified with conc. HCl with stirring. Under the conditions used, the yellow form of tungstic acid, H_2WO_4 was formed on the TiO_2 support. The resultant solid was centrifuged, washed several times with double distilled water and heated at the following temperatures for varying periods of time in air : 250°C, 500°C, 750°C, and 1000°C. A sample dried at room temperature (25°C) was also used for subsequent irradiation experiments.

Characterisation of the Catalysts

X-ray powder diffraction measurements were carried out with a Shimadzu XD 7A model diffractometer with CuKα radiation. The reflectance spectra of the samples were obtained using the full integration sphere of a Shimadzu model 365 UV-VIS spectrophotometer. Differential thermal analysis measurements were performed on a Shimadzu model DT-40.

Photochemical reactions in aqueous suspensions

WO_3/TiO_2 catalysts prepared under different conditions (calcination temperature, heating time and the % of WO_3 loaded on TiO_2) were suspended in 100 ml of water in an immersion well type photochemical reactor (Applied photophysics, UK) of 125 ml capacity. The water was freshly distilled from an all glass still. For each run 0.200 g of the composite catalyst was employed. The N_2 used was purified by passing through a hot copper pellet column, chromic acid solution, NaOH solution and finally H_2O. Effluent gases from the reactor were bubbled through a trap containing 10 ml of 0.1M HCl. The suspension in the reactor was magnetically stirred throughout the irradiation process. Irradiations were carried out using a 125W medium pressure mercury lamp housed inside a water cooled quartz jacket. The lamp emits $\geq 5 \times 10^{18}$ photons/s inside the reaction flask. The temperature of the solution was about 35° C under irradiation.

After irradiation, the mixture was treated with 10ml of 0.2M NaOH and the ammonia in solution was distilled into the trap containing 10 ml of 0.1M HCl. The ammonia in the distillate was determined colorimetrically by the indophenol blue method[8]. The nitrate content of the solution was determined colorimetrically by the coupling reaction of sulphanilic acid with N-(1-naphthyl) ethylene diamine after cadmium reduction. Control experiments were carried out under dark and also under argon under identical experimental conditions.

Photochemical reactions in the gas phase

An aqueous slurry of the catalysts prepared under different conditions was coated on the inside of the reactor vessel by means of a rotavapor. The resultant solid coating was heated under water aspirator vacuum in a steam bath for 1h. Irradiation procedure was

similar to the one described above for the aqueous suspensions. After irradiation, 100 ml of distilled water was first added and stirred well before analyzing for NH_3 and NO_3^-.

Results and Discussion

Characterization of the Catalysts

X-ray diffraction analysis show that when TiO_2 (anatase) powders were treated with Na_2WO_4/HCl, and the resultant solids heated at 250°C, the tungsten species deposited on TiO_2 is the yellow tungstic acid, H_2WO_4 (ASTM 2-0395). On the other hand, composite WO_3/TiO_2 catalysts prepared at 500° C, 750° C and 1000° C all showed the presence of stoichiometric WO_3 (ASTM 20-1323) which is lemon yellow in colour. X-ray diffraction patterns of the composites also show that there has been a total conversion of the anatase to the rutile form at 1000° C.

Differential thermal analysis measurements on the composite catalysts showed that the water loss from the adsorbed tungstic acid. $WO_3.H_2O$ takes place at 415° C. Reflectance spectra in the 200-800 nm range indicate a gradual extension of the absorption inflexion to the visible region upon heating at higher temperatures.

Photochemical reactions in aqueous suspensions

The following variables in the preparation of the catalyst which affect the yield of photosynthetically produced NH_3 were investigated independently: calcination temperature, duration of heating and the % (w/w) of WO_3 on TiO_2. The effect of pH variation on the yield of NH_3 was also investigated. It was found that the optimum pH for this reaction is between 5-6 (Figure 1) and at pH values ≥ 7, the adsorbed tungsten oxide dissolves.

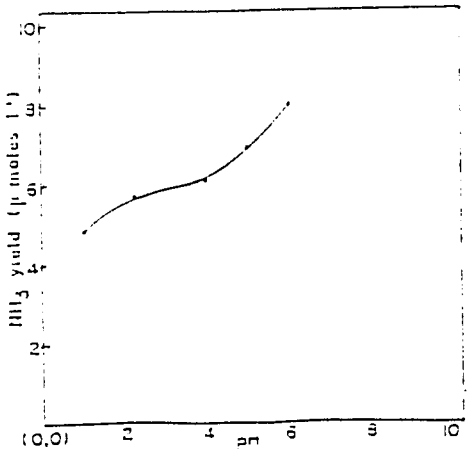

Fig 1. Variation of NH_3 yield with pH for the WO_3/TiO_2 (15% w/w) system.

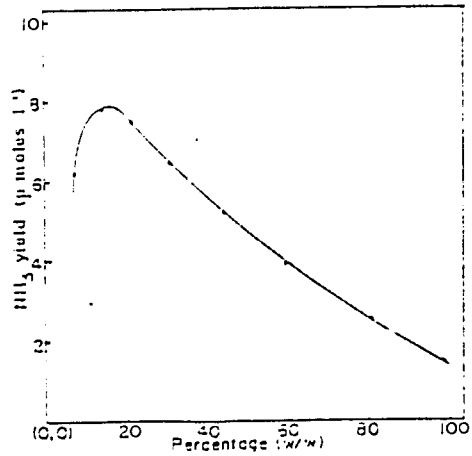

Fig 2. Variation of NH_3 yield with the amount of dopant for the WO_3/TiO_2 system.

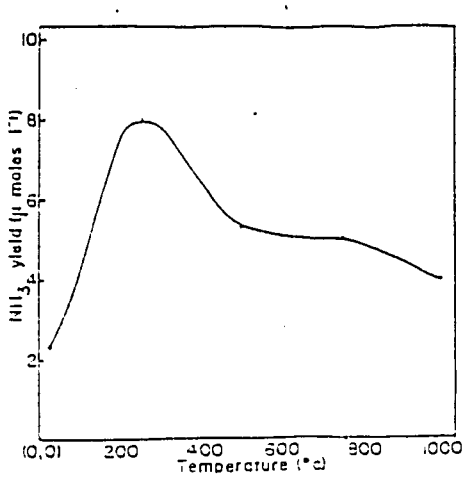

Fig 3. Variation of NH_3 yield with heating temperature for the WO_3/TiO_2 (15% w/w) system.

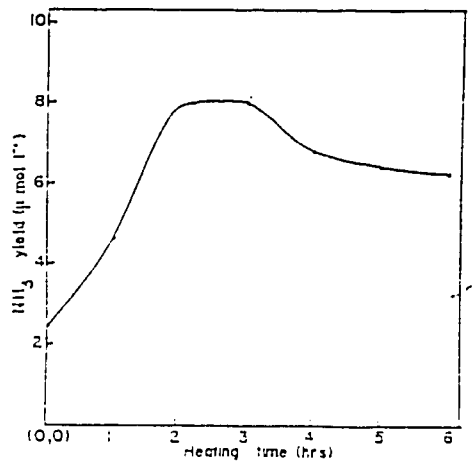

Fig 4. Variation of NH_3 yield with heating time for the WO_3/TiO_2 (15% w/w) system.

It was found that the highest yield of NH_3 was observed at a dopant level of 15% (w/w) of WO_3 coated on TiO_2 (Figure 2). Figures 3 & 4 give the effect of calcination temperature and heating time on the NH_3 yields at a dopant level of 15%. It is seen that heating at 250° C gives the best photocatalyst for the above reaction. At higher temperatures, particle sizes increase and the resultant loss in effective contact area could affect the reduction of WO_3 via the injection of photogenerated electrons on the TiO_2 semiconductor (Equations 2 & 3).

$$TiO_2 \xrightarrow{h\nu} TiO_2^{*}(h^+, e^-) \qquad (2)$$

$$W(VI) \xrightarrow{e^-} W(V) \qquad (3)$$

Interestingly, physically mixed powders of TiO_2 and WO_3 do not show any colour changes nor any photocatalytic activity upon irradiation. This observation too shows the importance of proper surface contact for the photoinduced reduction of WO_3 by TiO_2. Irradiation of the stoichiometric WO_3 in the absence of TiO_2 does not produce any reduction to the blue oxide.

At 250° C, X-ray diffraction data indicate that the TiO_2 is completely in the anatase form while the tungsten species is present as the amorphous yellow tungstic acid, $WO_3.H_2O$. At 500° C however, the adsorbed tungsten oxide is crystalline and X-ray analysis indicate this to be stoichiometric WO_3 with a triclinic structure (ASTM 20-1323).

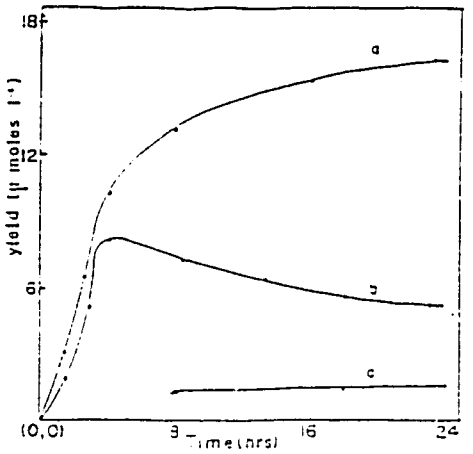

Fig 5. Variation of NH_3 and NO_3^- yields with time for the WO_3/TiO_2 (15% w/w) system, (a) gas-solid phase (NH_3), (b) aqueous suspension (NH_3) (c) aqueous suspension (NO_3^-)

The variation of NH_3 and NO_3^- formation with time for the sample which gave optimum yields (15% w/w WO_3, heating temperature 250° C, heating time 2h and a pH of 6) is given in Figure 5.

The NH_3 yield observed (8 μmole l^{-1}) after 6h of irradiation was much higher than the values reported in the literature for other related metal ion doped TiO_2 catalyst systems. It is also seen that NO_3^- formation is not observed up to 6h of irradiation which thereafter recorded only a slow increase. This again illustrates the detrimental effects of nitrate formation on the photoreduction of N_2 to NH_3.

During irradiation, the pale yellow composite mixture turns pale blue quite rapidly but within about one hour this completely changed to an intense blue colour. A similar observation has been noted by Bard et.al upon irradiating films of WO_3 deposited by vacuum deposition. This has been attributed to the formation of a tungsten bronze (equation 4)

$$WO_3 + yH^+ + ye^- \rightleftharpoons HyWO_3 \quad (4)$$

The rapid formation of this bronze which seems inactive toward N_2 reduction compared to the substoichiometric WO_{3-x} species explains the gradual loss of activity with time. Also, contrary to our expectations, a cyclic system for N_2 reduction using this system could not be developed owing to the formation of the inactive bronze. X-ray diffraction analysis confirmed bronze formation.

There is simultaneous oxidation of H_2O to O_2 while N_2 is reduced to NH_3 on the semiconductor. We have earlier shown that oxidation of the ammonia with O_2 eventually gives rise to NO_3^-. Figure 5 shows how the lowering yields of NH_3 with time is related to

increasing yields of NO_3^-. It is generally believed that hydroxyl free radicals produced on the surface of the semiconductor are involved in the oxidation of NH_3 (Equations 5 & 6).

$$TiO_2 \xrightarrow{h\nu} TiO_2 \cdot (h^+, e^-) \qquad (5)$$

$$OH^-_{ads} + h^+ \longrightarrow OH^{\cdot}_{ads} \qquad (6)$$

Dark controls where N_2 was passed through the catalyst for an identical period of time and also where N_2 was replaced by argon produced no appreciable amounts of NH_3 (< 0.1 μmole) or NO_3^- (< .05 μ mole). Thus with this catalyst preparation where initially only stoichiometric yellow form of WO_3 is present, no NH_3 is produced via a thermochemical pathway.

Photochemical reactions in the gas/solid phase

The sample selected for solid state studies was the one which gave highest yields of NH_3 in solution (15% (w/w) WO_3/TiO_2, heating temperature 250° C, heating time 2h, pH, 6). There were some notable differences between the gas/solid phase reaction and the reactions in aqueous suspensions (Fig.5). The NH_3 yields were significantly higher than for aqueous suspensions. The NO_3^- yields observed in the solid state were very small compared to the values observed for aqueous suspensions. In the solid state the adsorbed hydroxyl ions may be the limiting factor which prevents photooxidation of NH_3 to NO_3^-. The yields of NH_3 reach a maximum after 16h of irradiation and remains constant thereafter. The NO_3^- once formed could block the catalytic sites available for NH_3 synthesis and this could explain the decreasing NH_3 yields in solution. In the solid state, only a pale blue colour appears during irradiation and there is no evidence for any bronze formation.

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TiO_2 AND WO_3 SEMICONDUCTOR PARTICLES IN CONTACT: PHOTOCHEMICAL REDUCTION OF WO_3 TO THE NON-STOICHIOMETRIC BLUE FORM

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ABSTRACT

Hydrous tungsten oxide $WO_3.xH_2O$ in contact with TiO_2 grains suspended in water is found to get reduced $WO_{2.96}.xH_2O$ upon irradiation with uv light. Measurement of the band position of $WO_3.xH_2O$ suggests that electron transfer from TiO_2 to $WO_3.xH_2O$ is responsible for the reduction.

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INTRODUCTION

Recently, the properties of semiconductor particles and their photocatalytic activity has aroused much interest. The photocatalytic activity of semiconductor particles depends on injection of photogenerated carriers to the solution. It is known that the reduction in size of the particle, surface modifications, deposition of noble metals and other semiconducting materials enhance the charge separation improving the catalytic activity.[1-3] A composite catalyst consisting of two semiconductor particles in contact is of special interest, because of the availability of large number of semiconducting materials with different band gaps and band positions. Several authors have noted the catalytic properties of such composite systems and attributed this activity to the enhanced charge separation.[1-6] In this note we give an example that vividly demonstrate light induced charge separation in a composite semiconductor particle. Tungsten oxides of oxygen stoichiometry less WO_3 are known to possess a deep blue colour.[7] We have found that when WO_3 oxide particle in contact TiO_2 is irradiated in the presence of water a deep blue colour is developed as a result of electron transfer from TiO_2 to $WO_3.xH_2O$.

EXPERIMENTAL

Composite particles (where TiO_2 and WO_3 are in contact) was prepared as follows. 2g of TiO_2 is dispersed in 50 ml of 0.1M sodium tungsten solution. When excess dil. HCl is gradually added, tungstic acid (H_2WO_4) gets precipitated around the TiO_2 grains. The precipitate is filtered washed and dried in air at 250, 500, 750 and 1000°C for 2h are yellow in appearance. 200 mg of the $TiO_2/WO_3.xH_2O$ was suspended in 150 ml of distilled water in an immersion well type photochemical reactor (Applied Photophysis). The dispersion was

purged with N_2 to remove dissolved oxygen and then irradiated with a 125 W medium pressure Hg arc lamp. $WO_3.xH_2O$ (prepared by heating H_2WO_4 to 250°C for 2h) was compacted into pellets (diameter - 13 mm, thickness ~ 1mm, pressure - 40 MPa) were used to obtain the Mott-Schottky plots. Hewlett Packard LCR meter 4192A and Kenwood DL 707 Digital multimeter were used to measure capacitance and voltage respectively. X-ray diffractometry studies were done for the characterization of the catalyst (Shimadzu XD 7A model diffractometer with Cu K α radiation).

Results and Discussion

When the lamp was switched on for about 0.5 h, originally white suspension acquired a deep blue colour. The spectra (Shimadzu UV-3000 UV-Vis spectrophotometer) of the suspension before and after irradiation is compared in Fig.1. X-ray diffractometry data revealed (Fig. 2) that the blue colour corresponds to the non-stoichiometric compound $WO_{2.96}xH_2O$. The maximum reduction of $WO_3.xH_2O$ to $WO_{2.96}xH_2O$ was observed with the powder mixture heated up to 250°C for 2h. This is probably due to the formation of good surface contacts between TiO_2 and WO_3. The physically mixed TiO_2 (anatase) and WO_3 powders heated to 250°C for 2h did not show the reduction. This observation indicates the necessity of efficient surface contacts.

X-ray diffractometry data showed that drying at 250°C for 2h produces amorphous $WO_3.xH_2O$. The differential thermal analysis (Shimadzu model DT 40) data confirmed that the bound water in $WO_3.xH_2O$ begins to loose at about 415°C. The other materials (heated up to 500, 750 and 1000°C for 2h) was crystalline WO_3, lemon yellow in colour.[8]

The diffuse reflectance spectra of $WO_3.xH_2O$ (Fig. 3) suggested that the band gap of the material ~ 3.15 eV. The flat-band potential of $WO_3.xH_2O$ derived from the Mott-Schottky plots (Fig.4) is -0.45V [V vs SCE] at pH 5.5. The relative band positions of the TiO_2 and $WO_3.xH_2O$ is shown in Fig.5. The band position of TiO_2 at pH 5.5 known to be -0.7 V [V vs SCE].[9] As conduction band of $WO_3.xH_2O$ situated below the conduction band of TiO_2, photogenerated electrons will be transferred to the conduction band of WO_3, while holes accumulate in TiO_2. In the presence of water electron could participate in the reaction

$$25WO_3.xH_2O + H_2O + 2e^- \longrightarrow 2OH^- + 25WO_{2.96}.xH_2O \quad (1)$$

CB WO_3

Holes that accumulated on TiO_2 will generate OH^- free radicals at the surface of Ti_2O grains

$$OH^- + h^+ \longrightarrow OH^\circ \quad (2)$$

VB TiO_2

Oxygen evolution is not detected, as expected. This could result from the formation of peroxo-complexes of titanium.[10] When the photoproduced blue compound is exposed to oxygen rapid bleaching is observed as a result of oxidation to the stoichiometric oxide.

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FIGURE CAPTIONS

Fig. 1 The diffuse reflectance spectra of (a) TiO_2 (b) TiO_2/WO_3 (c) $TiO_2/WO_{2.96}$ (d)$WO_3.xH_2O$

Fig. 2 The relative band positions of TiO_2 and $WO_3.xH_2O$ at pH 7. Energies are given in eV with respect to the standard calomel electrode (SCE)

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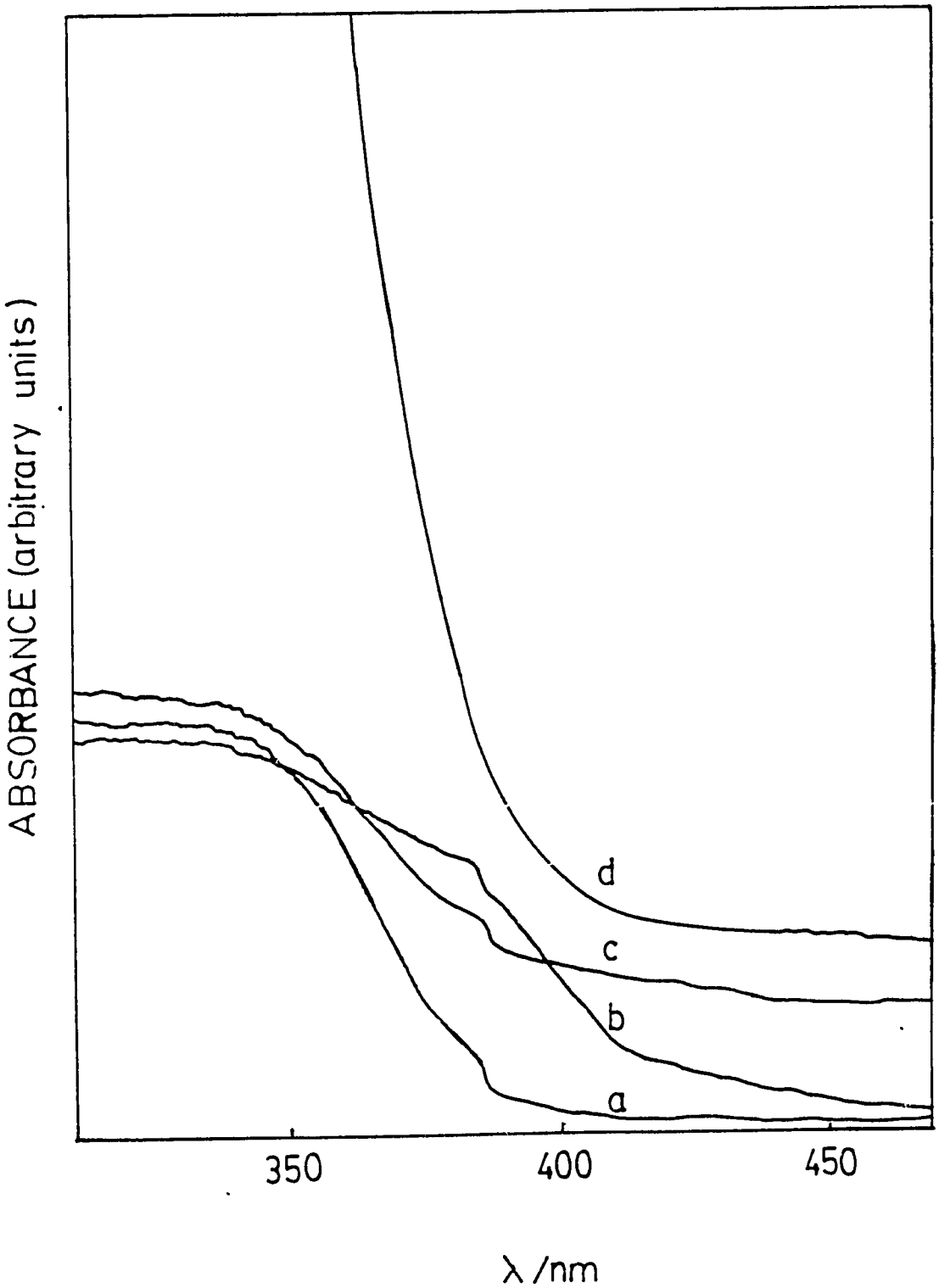

Fig. 1

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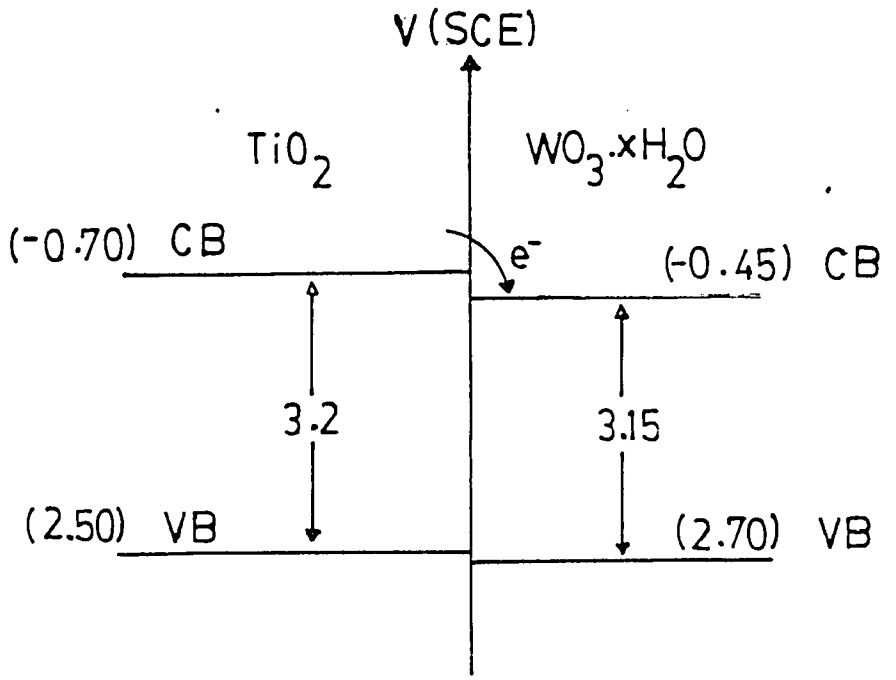

Fig. 2

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PHOTOREDUCTION OF N_2 TO NH_3 ON THE COMPOSITE CATALYST OF MoO_3/TiO_2

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ABSTRACT

Molybdenum/TiO_2 catalyst is active than the earlier reported M/TiO_2 systems where M = Fe, Ru, Co, Ni. The catalytic activity depends on a number of variables in the catalyst preparation. Irradiated TiO_2 reduces MoO_3 to $MoO_{2.5}$ and the reduced Molybdenum species converts N_2 to NH_3. Some NH_3 formed is photooxidized to NO_3^-. Irradiation for longer periods results in bronze formation and loss of photocatalytic activity.

INTRODUCTION

Photocatalytic nitrogen fixation reactions on semiconductors have attracted considerable attention as a possible way of solar energy conversion[1]. Although a large number of metal doped TiO_2 catalysts[2,3] have been investigated for this purpose, the yields are too small to be of any practical significance. Furthermore, the catalytic activity deteriorates with time owing to back reactions and catalyst poisoning.

Bard has shown that the reaction of moist N_2 on blue tungsten oxide in the solid phase containing $WO_{2.96}$ gives ammonia in a thermal reaction[4].

$$WO_{2.96} + 0.04H_2O + (0.04/3)N_2 \text{-------}> WO_3 + (0.08/3)NH_3$$

The potential of utilizing this reaction to devise a cyclic path way for N_2 fixation arose from our observation[5] that irradiated TiO_2 reduces WO_3 to the substoichiometric reduced form presumed to have the formula $WO_{2.96}$. We have found that although the system WO_3/TiO_2 is active for N_2 fixation, an efficient cyclic pathway could not be realized due to the formation of an inactive bronze.

In a continuation to study such a cyclic system we have studied the catalyst system MoO_3/TiO_2 which behaves in a similar manner. A catalyst consisting of two semiconductor particles in contact is of special interest, because of the availability of a large number of semiconductor materials with different band gaps and band positions. Several authors have noted the catalytic properties of such composite systems and their activities to enhance charge separation [6].

EXPERIMENTAL

TiO_2 powder was dispersed in distilled H_2O and the calculated amount of MoO_3 was added and stirred for 3 hours and the yellow coloured powder was evaporated to dryneess. The resultant solid was calcined at 250, 500, 750 and 1000°C for 2h. 200 mg of the yellow coloured TiO_2/MoO_3 catalyst was suspended in 350 ml of distilled H_2O in an immersion well type photochemical reactor (Applied photophycis). The dispersion was purged with N_2 to remove dissolved O_2 and was irradiated with a 400 W medium pressure Hg arc lamp. The lamp emits > 7 x 10^{19} photons S^{-1} inside the reaction flask.

Effluent gases from the reactor were bubbled through a trap containing 10 ml of 0.1 M HCl. The suspension in the reactor was magnetically stirred throughout the irradiation. Control experiments were carried out under N_2 in the dark and also under irradiation with argon.

After irradiation, the mixture in the reactor flask was treated with 10 ml of 0.2 M NaOH and the ammonia in solution was distilled into the trap containing 10 ml of 0.1 M HCl. The ammonia in the distillate was determined colorimetrically by the indophenol blue method[7]. The nitrate content of the solution was determined colorimetrically by the coupling reaction of sulphanilmide with N-(1-napthyl)ethylenediamine dihydrochloride after cadmium reduction.

Characterization of the Catalysts

X-ray powder diffraction measurements were carried out with a Shimadzu XD7A model diffractometer with Cuk radiation. The reflectance spectra of the samples were obtained using the

full integration sphere of a Shimadzu model 365 UV-Vis spectrophotometer. Catalyst powders compacted into pellets (diameter 13 mm, thickness 108 /mm, pressure 40 mpa) were used to obtain the Mott-Schottky plots. Hewlett Packard LCR meter 4192A and Kenwood DL 707 Digital multimeter were used to measure capacitance and voltage respectively.

RESULTS AND DISCUSSION

The variation of the ammonia yield with percentage (w/w) variation of MoO_3 on TiO_2 was done and it was found that the composite catalyst having 50% (w/w) had the highest N_2 reduction ability. It was observed that calcination at 750°C gives the maximum ammonia yield. X-ray powder diffraction pattern showed the presence of MoO_3, H_2MoO_2 and a small amount of a reduced oxide $[MoO_{2.5}(OH)_{0.5}]$ in the catalyst which was calcined at 750° and XRD quantitative analysis showed that 9% of Molybdenum has been incorporated into the TiO_2 lattice and the remainder is present as crystalline MoO_3 in the catalyst. Further heating upto 1000°C shows the phase change of TiO_2 from anatase to rutile form which is catalytically less active.

Physically mixed TiO_2 and MoO_3 catalyst showed very little ammonia yield. This observation indicates the necessity of efficient surface contacts for this reaction. It was observed that even the calcination time is important to get the best surface contacts, in this case the best heating time was 2h.

The diffuse reflectance spectra of MoO_3 suggest that the band gap of MoO_3/TiO_2 is 2.98 eV. As there is very little NH_3 yield in the presence of a UV cutoff filter it was confirmed that the composite catalyst absorbs mostly in the UV region.The flat-band potential of MoO_3 derived from the Mott-Schotkey plots (E_{CB}) is -0.6eV (vs SCE) at pH 3. The conduction band position (CB) of TiO_2 at pH 3 is known to be at 0.6eV (vs SCE).

TiO_2 absorbs the light and charge separation occurs on TiO_2. Because CB of MoO_3 is situated below the CB of TiO_2, photogenerated electrons will be transferred to the CB of MoO_3, while holes accumulate in TiO_2.

$$h\nu + TiO_2 \longrightarrow TiO_2^{+}(h^{+},e^{-})$$

$$e^{-}_{CB} + Mo(VI) \longrightarrow Mo(V)$$

Holes that accumulate on TiO_2 will generate $OH^{\cdot}$ at the surface of TiO_2 grains.

$$OH^{-} + h^{+} \longrightarrow OH^{\cdot}$$

During the irradiation, the pale yellow composite mixture turns pale blue quite rapidly, but within about one hour this completely changes to an intense blue colour. The X-ray powder diffraction pattern of the sample after one hour of illumination showed the presence of a bronze $H_{0.3}MoO_{2.7}$ and $MoO_{2.5}(OH)_{0.5}$ (molybdenum blue). There is still no satisfactory explanation for the origin of the blue colour in these molybdenum bronzes molybdenum in this compound has an average oxidation state between 5 and 6. The bronze itself and the reduced Molybdenum oxide are not photoactive[9].

During irradiation Mo(vi) is reduced to the Mo(v) state.

$$e^{-}_{CB} + Mo(vi) \longrightarrow Mo(v)$$

As with $WO_{2.96}H_2O$, reduced Molybdenum oxide is capable of fixing N_2 thermally. The observation of N_2 reduction by chemically reduced Molybdenum oxide confirms the thermal pathway for the N_2 reduction to NH_3. The reduction of N_2 to NH_3 occurs at reduced Molybdenum [Mo(v)] centers as follows.

$$0.5/2\ N_2 + MoO_{2.5}(OH)_{0.5} + H_2O \longrightarrow MoO_3.H_2O + 0.5\ NH_3$$

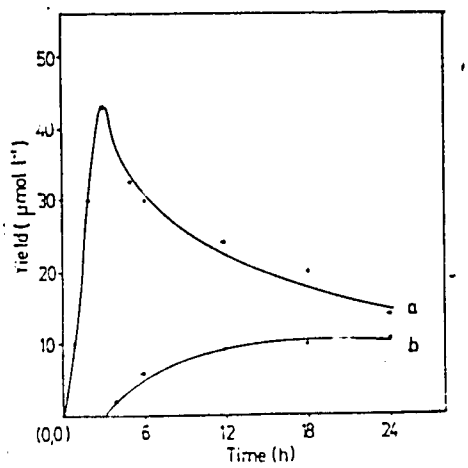

Fig.1 Variation of (a) NH_3 (b) NO_2^- with irradiation time for the MoO_3/TiO_2 (50% w/w Mo) system.

Dark controls where N_2 was passed through the catalyst for an identical period of time and also where N_2 was replaced by Ar produced no appreciable amounts of NH_3 or NO_3^-.

It is seen that the optimum NH_3 yield is obtained at a pH of 3. . At very low pH values ammonia yield is smaller and this can be attributed to the enhancement of bronze formation, for pH values > 9 MoO_3 dissolves giving soluble molybdate.

Time variation of ammonia production for the catalyst prepared under optimal conditions is given in Fig.1. This shows that the NH_3 yield increases upto 4hr (45umol l^{-1}) and thereafter decreases. In the mean time an increase in NO_2^-/NO_3^- concentration was also observed. This may be due to the :-

(1). Oxidation of NH_3:-

$$4NH_3 + 5O_2 \longrightarrow 4NO + 6H_2O$$
$$NO + O_2 \longrightarrow NO_2$$

(2). Rapid formation of the bronze which seems inactive toward N_2 reduction compared to the sub stoichiometric Molybdenum species explains the gradual loss of activity with time.

Also , contrary to the expectation, a cyclic system of N_2 reduction using this system could not be developed owing to the formation of the inactive bronze.

As the CB of Mo/TiO_2 lies above the reduction potential of H_2O (-0.6), H_2 evolution is possible and H_2 was detected by GC under Ar and N_2 in a closed system. Yields were lower than

expected. This may be due to the consumption of H_2 on reducing centers to produces the bronze. H_2 evolution under Ar is greater than that of under N_2. Under N_2, H_2 is used for ammonia formation. Oxygen determination using a membrane polorographic detector showed only a trace amount of O_2. As the CB lies below the H_2O oxidation potential level O_2 formation is possible. Holes in the VB are trapped by H_2O and OH^- to produce O_2.

$$2OH^- + 4h^+ \longrightarrow O_2 + 2H^+$$
$$2H_2O + 4h^+ \longrightarrow O_2 + 4H^+$$

The very low yield of O_2 may be due to the consumption of O_2 to oxidize the reduced Mo(v) centers. When the photoproduced blue compound is exposed to O_2 very slow bleaching is observed as a result of oxidation to the stoichiometric oxide, MoO_3.

ACKNOWLEDGEMENT

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Photoreduction of nitrogen dissolved in water with hydrous oxides of samarium (III) and europium (III)

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The hydrous oxides of samarium (III) and europium (III) are found catalyse photoreduction of dinitrogen dissolved in water. It is suggested that their activity depends on chemisorption of nitrogen and sufficiently negative flat band potential.

1. Introduction

A number of semiconductor materials in the particulate form are known to photogenerate hydrogen from water with concomitant oxygen evolution and/or formation of adsorbed oxygen [1–4]. In the presence of a sacrificial electron donor, the quantum yield of hydrogen evolution is greatly increased [1]. Few semiconductor photocatalysts are also known to have the ability to reduce dinitrogen dissolved in water [5–17]. Aqueous dispersions of TiO_2 are found to photogenerate less hydrogen when purged with nitrogen than argon. This was proved to result from some reduction of dinitrogen to ammonia. The photocatalytic reduction of dinitrogen to ammonia even at modest conversion efficiencies is of tremendous practical importance. If such a method is available, sunlight could be used to supplement irrigation waters with ammonia. Unfortunately, the photocatalytic nitrogen reduction is even more difficult to achieve than water photodecomposition, for the following reasons.

(1) The reduction of one molecule of dinitrogen via

$$\begin{aligned} &N_2 + 6\,H^+ + 6\,e^- \rightarrow 2\,NH_3, \\ &3\,H_2O + 6\,h^+ \rightarrow \tfrac{1}{2}O_2 + 6\,H^+, \end{aligned} \tag{1}$$

involves transfer of six electrons, compared to two electrons in the reduction of water, i.e.,

$$\begin{aligned} &2\,H_2O + 2\,e^- \rightarrow H_2 + 2\,OH^-, \\ &2\,OH^- + 2\,h^+ \rightarrow H_2O + \tfrac{1}{2}O_2. \end{aligned} \tag{2}$$

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Generally each photon transfers a single electron and the probability of six photons concentrating on one molecule is highly improbable.

(2) In the water photodecomposition reactions, the multi-electron transfer can be enhanced by loading the catalyst with platinum or other noble metals. In the case of nitrogen reduction, loading the catalyst with platinum interferes with nitrogen chemisorption. (In a platinum-coated catalyst, the reductions take place on platinum-coated sites. Nitrogen is poorly chemisorbed on platinum.)

(3) Photogenerated ammonia accumulates in the solution and participates in back reactions, e.g. oxidation to nitrogen, nitrite or nitrate.

(4) Unlike in water photodecomposition to hydrogen, the sacrificial electron donors generally does not increase the quantum yield. A likely reason is that the sacrificial agent interferes with nitrogen chemisorption.

(5) Dinitrogen chemisorption is a necessary requirement for catalytic activity. Most semiconductor catalysts that have sufficiently negative flat band potentials chemisorb dinitrogen poorly.

In order to increase the quantum yields of nitrogen reduction, it is necessary to search for new catalytic materials that chemisorb nitrogen strongly and at the same time having sufficiently negative flat band potentials. The spatial separation of oxidation and reduction sites in such a way that the reductions take place on nitrogen chemisorbing region would further enhance the quantum yields [16]. We have noted earlier, that the hydrous ferric oxide photocatalyst gives relatively higher yields of ammonia [10]. After examining a large number of other stable hydrous oxides we have noted that those of samarium (III) and europium (III) are also active towards photoreduction of nitrogen to ammonia. The yields are greater than those obtained with hydrous ferric oxide [10] under similar conditions.

2. Experimental

Hydrous samarium (III) and europium (III) oxides were prepared by gradual addition of excess 0.05M NaOH to a 0.05M solution of respective chlorides kept vigorously stirred. The semi-transparent gel of the hydrous oxide was washed and separated by centrifuging. As these catalysts denature upon drying and cannot be weighed, the volume of solution used to make the precipitate was taken as a measure of the catalyst employed. The catalyst made from 25 ml of XCl_3 (X = Sm or Eu) was dispersed in a thermostatted (26°C) immersion-well-type photochemical reactor of volume 300-ml. A medium pressure mercury lamp (400 W) mounted at the central axis of the reactor was the irradiation source. During photolysis the solution (275 ml) in the reactor was kept continously purged with nitrogen (99.999%) at a bubbling rate of 120 ml min^{-1}. The solutions subject to irradiation for different intervals of time were made strongly alkaline with NaOH and distilled. Ammonia concentration in the distillate was esumated spectrophotometrically by the indophenol blue method. The residue was tested for nitrate and nitrite. All reagents used were tested for ammonia and nitrate. When the experiment was carried out in

dark with N_2 purging, the level of ammonia observed was taken as the zero standard. Furthermore, the ammonia concentration obtained when the solution was irradiated while purging argon came close to the above zero standard. Hydrogen evolution during photolysis was determined by gas chromatography (Shimadzu GC-9AM gas chromatograph: carrier gas Ar). Oxygen evolution was tested by carrying out photolysis in a reaction vessel provided with a polarographic detector (Applied Photophysics) for monitoring the oxygen concentration. This method is more reliable as gas chromatography always leads to some atmospheric oxygen contamination.

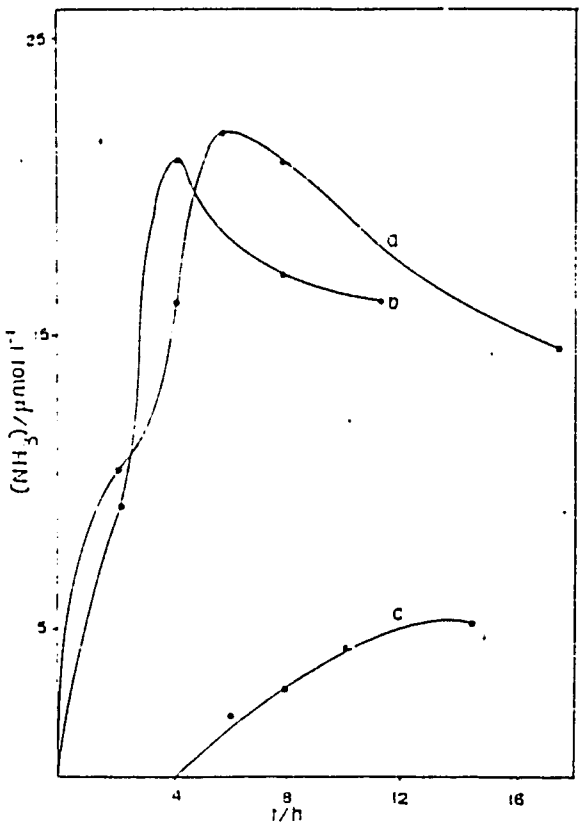

Fig. 1. Time variation of the ammonia yield at pH 10 from (a) $Sm_2O_3 \cdot [H_2O]_n$, (b) $Eu_2O_3 \cdot [H_2O]_n$; (c) nitrate yield from $Eu_2O_3 \cdot [H_2O]_n$ (the catalyst used was made by hydrolysis 25 ml of 0.05M solutions of Sm(III) and Eu(III) chlorides).

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3. Results and discussion

Fig. 1 shows the yield of ammonia from the catalysts $SmO_3 \cdot [H_2O]_n$ and $Eu_2O_3 \cdot [H_2O]_n$ when the pH of the solution is ~ 10. The optimum yields were obtained at this pH. Existence of an optimum pH can be understood. Thermodynamically, the N_2 reduction reaction is favoured by a high concentration of H^+ ions (i.e., low pH). However, the flat band potential increases in the negative direction favouring N_2 reduction at higher pHs. These two opposing effects lead to an optimum pH.

The same behaviour is seen in nitrogen reduction with other semiconductor catalysts [10]. A feature common to both catalysts is, that the ammonia concentra-

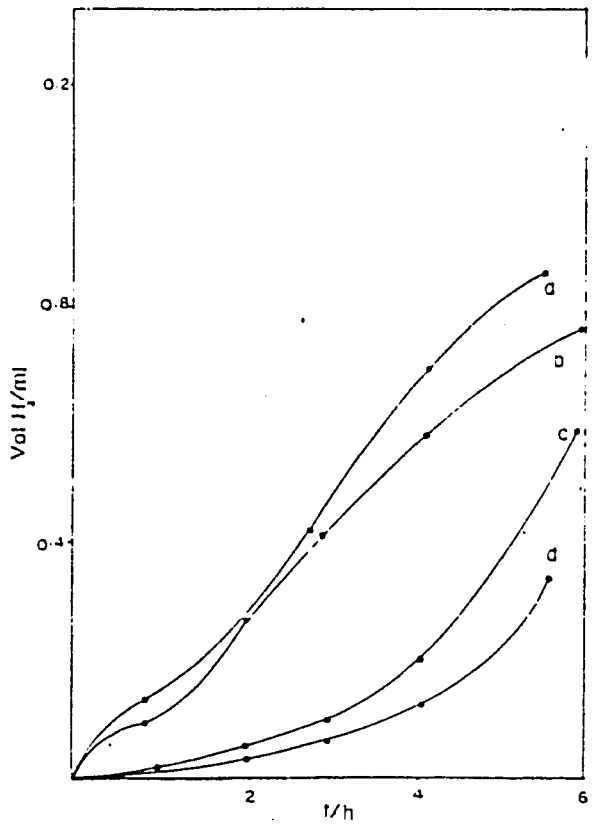

Fig. 2. Hydrogen photogeneration from aqueous suspensions of (a) $Sm_2O_3 \cdot [H_2O]_n$ saturated with Ar, (b) $Sm_2O_3 \cdot [H_2O]_n$ saturated with N_2, (c) $Eu_2O_3 \cdot [H_2O]_n$ saturated with Ar, (d) $Eu_2O_3 \cdot [H_2O]_n$ saturated with N_2 (the quantity of catalyst used as in given in the caption of fig. 1).

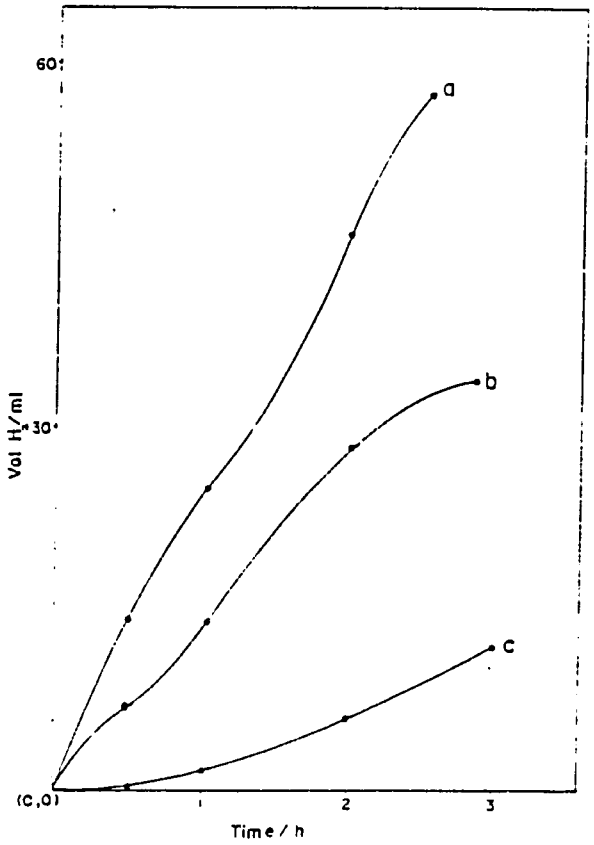

Fig. 3. Hydrogen photogeneration from 20% solution of ethanol with the catalysts (a) $Sm_2O_3 \cdot [H_2O]_n$, (b) TiO_2, (c) $Eu_2O_3 \cdot [H_2O]_n$.

tion in the solution rapidly increases, reaches a maximum in about 4–6 h and then gradually decreases (fig. 1). The nitrate concentration in the solution shows opposite behaviour (Fig. 1); in the initial phase it is negligible and then rapidly increases with a concomitant decrease in the ammonia concentration. In the experiments with the polarographic detector, a feeble oxygen signal is detectable, but the yield is far below the stoichiometry of eq. (1). This indicates that the photogenerated oxygen is preferentially adsorbed on the catalyst. Presumably, nitrate is generated via oxidation of ammonia by the adsorbed oxygen. Both catalysts liberate hydrogen from water under irradiation, argon saturated solutions give higher yields than nitrogen purged solutions as expected (fig. 2). Under sacrificial conditions (e.g., in the presence of ethanol), the hydrogen yield is drastically increased (fig. 3). In fact $Sm_2O_3[H_2O]_n$ is even superior to TiO_2 in this respect (fig. 3). Anhydrous oxides

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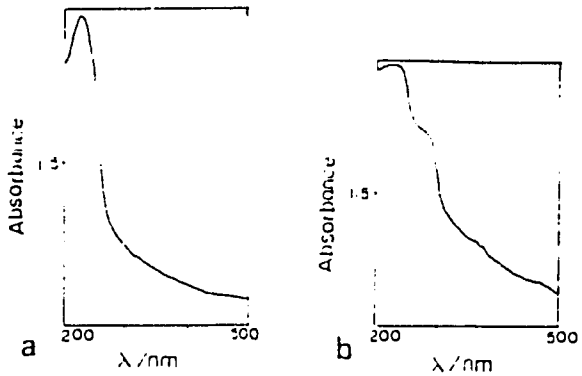

Fig. 4. Absorption spectra of aqueous suspensions of (a) $Sm_2O_3[H_2O]_n$ and (b) $Eu_2O_3[H_2O]_n$.

Sm_2O_3, Eu_2O_3 are found to be almost completely inactive towards N_2 reduction or H_2 photogeneration. Again upon platinization hydrous oxides loose photocatalytic activity. The absorption spectra of aqueous suspensions of the two hydrous oxides are shown in fig. 4. There is clear evidence for a absorption band edge at 330 and 290 nm, respectively, for $Sm_2O_3[H_2O]_n$ and $Eu_2O_3[H_2O]_n$. When the electrical onset potentials of two materials coated on platinum foil was investigated, they were found be slightly more negative than TiO_2 (anatase), indicating their ability to carry out H_2 photoproduction and N_2 photoreduction reactions. Undoubtedly just as the hydrous ferric oxide, these two materials are also chemisorbing dinitrogen well. Hydrous oxides having layered structure are known to adsorb dinitrogen and assists its reduction [18–21]. It has been suggested that in these materials, dinitrogen is initially reduced unstable diazene (N_2H_2). The layered structure of the hydrous oxide lattice is believed to allow entrance of N_2 but not free OH that rapidly attack diazene.

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4. Impact, Relevance and Technology Transfer

The research results from the project has created an awareness in the developing country in an important area of research for the future. Through national workshops and meetings, the results have been disseminated and generally these meetings have produced fruitful discussions. The interest in the project can be seen from the numerous requests received from prospective graduate students to work in this area.

Sri Lanka is a small country which has not reached the critical size as far as the number of scientists in any particular area is concerned. However through International publications, the results have been communicated to the International scientific community. It may take a while for the research to catch up in this area since there is still an abundance of cheap oil. Once the international community fully comprehends the seriousness of the energy crisis in the next century, research an alternate sources of energy such as solar energy conversion will assume increased importance.

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5 Project Activities/Outputs

5.1 List of publications from the project

1. Photoinduced oxidative nitrogen fixation reactions on semiconductor suspensions, O.A. Ileperuma, F.N.S. Weerasinghe and T.S. Lewke Bandara, Solar Energy Materials, (1989), 19, 409.

2. Photoreduction of nitrogen and water on Montmorillonite clays loaded with hydrous ferric oxide, O.A. Ileperuma, W.C.B. Kirirdena, W.D.D.P. Dissanayake, J. Photochem. Photobiol. A Chemistry, (1991), A59(2): 191-7.

3. Photocatalytic behaviour of metal doped Titanium dioxide. Studies on the Photochemical Synthesis of Ammonia on Mg/TiO_2 catalyst systems, O.A. Ileperuma, K. Tennakone and W.D.D.P. Dissanayake, Applied Catalysis, (1990), 62, L1.

4. Photoreduction of Dinitrogen to Ammonia by Ultra fine Particles of Fe(O)(OH) formed by Photohydrolysis of Iron(II) bicarbonate, K. Tennakone, J.M.S. Bandara, C.T.K. Thaminimulla, W.D.W. Jayatilake, U.S. Ketiperarachchi, O.A. Ileperuma and M.K.A. Priyadarshana, Langmuir, (1991) in press.

5. Simultaneous Reductive and Oxidative Photocatalytic Nitrogen fixation in Hydrous Iron(III) Oxide loaded Nafion films in aerated water, K. Tennakone, O.A. Ileperuma, J.M.S. Bandara, C.T.K. Thaminimulla and U.S. Ketipearachchchi, J. Chem. Soc. Chem. Commun., (1991), 579.

6. TiO_2 and WO_3 semiconductor particles in contact: Photochemical reduction of WO_3 to the non-stoichiometric blue form, K. Tennakone, O.A. Ileperuma, J.M.S. Bandara, W.C.B. Kiridena, J. Photochem. Photobiol. A. Chemistry (submitted for publication)

7. Photoinduced reduction of WO_3 by TiO_2 and its role on photochemical synthesis of NH_3, O.A. Ileperuma, W.C.B. Kiridena and J.M.S. Bandara, Proc. Second Int. Symp. Soild State Physics II, (Nova publishers, USA), (1990), in press

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8. Photoreduction of nitrogen dissolved in water with hydrous oxides of Samarium(II) and Europium(III), K. Tennakone, O.A. Ileperuma, J.M.S. Bandara, C.T.K. Thaminimulla, Solar Energy materials, (1991) in press.

9. Photocatalytic nitrogen fixation on semiconductors, O.A. Ileperuma in Proc. Third Int. Symp. Solid State Physics, (Nova Science publishers, USA, to be published).

10. Photoreduction of N_2 to NH_3 on the composite catalyst of MoO_3/TiO_2, O.A. Ileperuma, C.T.K. Thaminimulla, J.M.S. Bandara and W.C.B. Kiridena, Proc. Third Int. Symp. Solid State Physics, (Nova Science publishers, USA, to be published).

11. Reduction of N_2 to NH_3 by Ti^{3+} in aqueous media and its photoenhancement, O.A. Ileperuma and T.S. Lewke Bandara, J. Natl. Sci. Council Sri Lanka, (1990), in press.

12. Photoreduction of N_2 to NH_3 and H_2O to H_2 on metal doped TiO_2 catalysts (M= Ce, V), O.A. Ileperuma, C.T.K. Thaminimulla, W.C.B. Kiridena, Solar Energy Materials, (1991), submitted.

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5.2 Training

Training of graduate students in the areas of Photochemistry, Instrumental analysis and Computer programming.

(a)	Mr. J.M.S. Bandara	M.Phil (completed)
(b)	Ms. C.T.K. Tilakaratne	M.Phil (completed)
(c)	Mr. W.C.B. Kiridena	Ph.D (in progress)

These students have got a thorough training in all aspects of Heterogeneous Photocatalysis on Semiconductors, Advanced Instrumental Analysis, Computer programming and presenting results at symposia.

The following international workshops were held at the Institute of Fundamental Studies (not supported by the PSTC grant) during the duration of the grant where our students, principal investigator and collaborators participated.

1. Second International symposium on Solid State Physics May 15-20, 1989, Kandy, Sri Lanka.

2. Third International symposium on Solid State Physics April 22-27, 1991, Kandy, Sri Lanka.

In addition, the Principal Investigator participated in the following Workshops/study tours.

1. Workshop on "Lasers in Chemistry" held at the International Center for Science and Technology, Trieste, Italy, April 1989. (Support from UNIDO).

2. Workshop on "X-ray Crystallography of Natural Materials" held in Bangkok, Thailand, February 1990. (support from UNESCO).

3. Visits to the foreign collaborator's laboratory, (Dr. Arlon, J. Hunt, Lawrence Berkeley Laboratory, berkeley, California) in 1989 and 1991. These two visits also included several visits to different laboratories in the USA where there are active groups working in heterogeneous photocatalysis.

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6. Project Productivity

The project achieved the major objectives stated in the original proposal. One of the goals not addressed during the course of research was the use of $^{15}N_2$ isotope to establish nitrogen fixation work. This was thought not quite necessary since the scientific community accept photochemical N_2 fixation work with the right controls, such as experiments under dark and argon as indicative of positive proof of N_2 fixation.

7. Future work

Future work in this project will be continued both at the University of Peradeniya, Sri Lanka and the Institute of Fundamental Studies, Kandy, Sri Lanka from the available resources. Work planned include some actual field trials on some plant species exhibiting a sensitive response to nitrogenous species. Diversification of the area of research to other areas such as water purification, development of bactericides based on Br_2 and H_2O_2 will also be undertaken.

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9. Summary of Expenditure

Item	Total Allocated (US $)	Total Spent (US $)
Salaries	9000	8972.68
Equipment	82200	81970.65
Materials & Supplies	18560	19257.82
Travel	7500	7818.00
Administration of the Grant	12000	10008.00
Other indirect costs	200	1402.00
Total	129460	129428.72

10. ACKNOWLEDGEMENT

I wish to record my deep appreciation to the long standing collaboration of Prof K. Tennakone, Sumanasekara Chair of Natural Sciences, Institute of Fundamental Studies, Kandy, Sri Lanka. Our long discussions on scientific problems and new ideas from the very inception of this project have contributed immensely to its success. I also wish to thank Prof. Cyril Ponnamperuma, former Director of the Institute of Fundamental Studies for encouraging research in this area and also for having faith in the importance of the project however small the yields of ammonia were.

I wish to thank all my students, present and former for their hard work which made this possible and finally to Mrs. D. Yatawara for the fine secretarial assistance provided throughout this project.